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Depolymerization of Lignin for Biomass Processing in Ionic Liquids

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Dedication

To my family

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Depolymerization of Lignin for Biomass Processing in Ionic Liquids

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The University of Texas at Austin, 2012

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There is growing need for technologies to displace traditional petroleum resources. Towards this goal, lignocellulosic biomass is seen as a potential renewable resource for the production of fuels and commodity chemicals. One of the most difficult components of lignocellulose to process is lignin, which is a complex, amorphous aromatic polymer that acts as one of the structural components in plants. Ionic liquids are a class of compounds that are composed completely of anions and cations that, in some cases, can completely dissolve lignocellulosic biomass. The research performed for this dissertation aims to advance the technologies of lignocellulose processing through effective depolymerization of lignin in ionic liquids. Lignin fragments from this depolymerization could be used as a feedstock for further processing into aromatic commodity chemicals or polymers. Additionally, by removing lignin, biomass becomes much more accessible to enzymatic or chemical saccharification as a step towards fermentation into ethanol or other fuels.

Both base and acid catalyzed methods were explored, although the base promoted depolymerization of lignin in ionic liquids did not show much promise, as the reaction was never shown to be catalytic. Acidic routes towards lignin depolymerization were more successful. Using the acidic ionic liquid 1-H-3-methylimiazolium chloride, the ether linkages in lignin model compounds could be hydrolyzed with high yields. This

technology was also applicable to the whole lignin macromolecule. The mechanisms of this reaction, as well as the effects on lignin were explored with various neutral and acidic ionic liquids, using HPLC, GPC, NMR, FT-IR, and mass spectrometry for analysis of samples. To demonstrate the applications of this technique, pine wood was treated with the acidic ionic liquids to open the structure of the wood to enzymatic saccharification through the removal of lignin and hemicellulose.

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1.1 INTRODUCTION

Biomass is already the single largest source of renewable energy in the United States and has great potential for further utilization as a renewable resource [1]. Globally, the potential for sustainable biomass derived energy is 100 EJ/a, which is 30% of the 2003 global energy consumption [2]. The majority of biomass falls into the category of lignocellulosic biomass, so named because it is composed of three biopolymers: cellulose, hemicellulose and lignin. Agricultural lands in the United States can produce nearly 1 billion dry tons of biomass annually while still meeting food, feed, and export demands, while US forest resources can produce an additional 368 million dry tons [1]. Other forms of biomass, such as corn starch (840 million tons in 2010 worldwide [3] and 216 million tons corn annually in the US [4]), or simple sugars such as glucose, fructose, or sucrose may also prove to be important resources.

Currently, biomass has grown as a source of fuel and chemicals. Production of ethanol from biomass has seen rapid growth with the US and Brazil leading the world in bio-ethanol production. Corn based ethanol productions in the US has reached 13.9 million gal while Brazil produces 5.6 million gal of ethanol from the fermentation of sugar cane annually [5]. In the US, the Energy Independence and Security Act of 2007 mandated production and blending of ethanol as a biofuel, which has led to the large scale production of corn based ethanol [6]. Based on the availability of resources, other

substrates for fermentation can be used, as is the case with sugar cane in Brazil [7]. Cellulose is looked to as the next generation of substrates for ethanol production, using feed stocks such as switch grass, sugarcane bagasse, or corn stover as a cellulose source [8]. In order for the cellulose to ethanol conversion to work, biomass sources must be pretreated to make the structural carbohydrates accessible to saccharification in preparation for conventional fermentation into ethanol [9]. The pretreatment step has been the subject of considerable research. Steam explosion, ammonia treatment, dilute acid treatment, milling, and even treatment with ionic liquids have been explored as methods for preparing biomass for saccharification [10–14].

While fermentation into ethanol is one option for converting biomass into fuel, other catalytic processes have been investigated and developed for the utilization of biomass. Using algae as a means of production for both bio-oil and carbohydrates has been looked to as a next generation source of biomass products due the algae's high yield per cultivation area and ability to thrive in a wide range of conditions [15]. Conversion of biomass into bio-oil has received considerable attention. Both fast pyrolysis and syn-gas processes hold considerable potential for biofuel production [16], [17]. Catalyst development and application of petro-chemical technology is also an important subject in the field of biofuels [18]. Even the less technologically advanced method of burning biomass provides a significant source of energy. Residue from processing of biomass into food or consumer products and biomass harvested specifically for fuel are a significant source of energy and have a high sustainable potential that has not yet been

realized [2]. Further discussion of the current state of biomass processing is covered in a number of other articles [2], [15], [17], [19], [20].

One of the challenges in utilizing biomass in chemical processing for fuels or other products is that, in most cases, the biomass is insoluble in commonly used solvents. Ionic liquids (ILs) are a class of compounds that are composed completely of anions and cations and melt at temperatures below 100°C. Recently, it has been found that some ILs are effective for dissolution of many kinds of biomass. Some can even completely dissolve lignocellulosic biomass up to 25% by weight without chemical modification of the biomass occurring[21]. Based on this discovery, the research on the catalytic transformation of biomass in ionic liquids has increased markedly in recent years. The hope of this research is that the unique solvent properties of ionic liquids coupled with the potential of biomass as a renewable resource will lead to advances in the next generation of fuel and chemical production.

1.1.1 Biomass

The most common biomass source, lignocellulose, is the principal component of plant matter and is the largest renewable resource available [1]. Lignocellulose is composed primarily of three biopolymers: cellulose, hemicellulose, and lignin. Cellulose, which is the most abundant biopolymer in lignocellulosic biomass, is comprised of glucose monomers linked together through 1-4 glycosidic linkages. As shown in Figure 1.1, these chains of glucose hydrogen bond with the hydroxyl groups of neighboring cellulose molecules, providing a stable, crystalline structure to cellulose

fibers in cell walls [22]. Because cellulose is the single most abundant renewable resource available, there has been significant work in its utilization across a wide range of applications. While cellulose can be somewhat difficult to break into its component glucose units, there are a number of methods, such as enzymatic or acid catalyzed hydrolysis, that will convert cellulose into monosaccharides or short carbohydrate chains [23], [24].

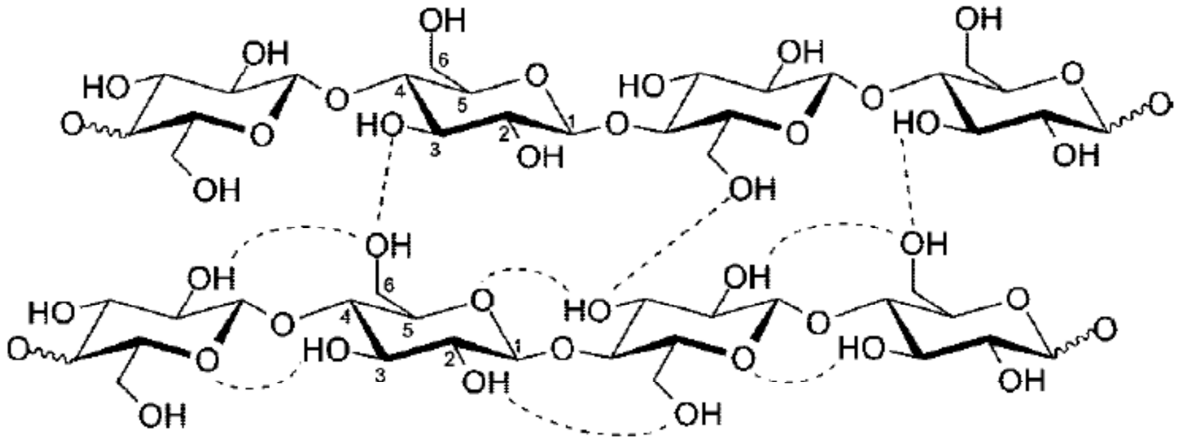

Figure 1.1: Intra- and intermolecular hydrogen bonds in cellulose [25].

Hemicellulose, which is similar to cellulose in that it is a polymer composed of monosaccharides, makes up 20 to 30% of plant biomass. Unlike cellulose, however, hemicellulose is a branched carbohydrate that can be made up of a various monosaccharides, bonded through a number of different glycosidic linkages. The structure of hemicellulose is composed of a polysaccharide backbone made from glucose, xylose, or mannose units connected through β-(1-3) or β-(1-4) glycosidic bonds. From these backbones, side chains of glucose, glucuronic acid, 4-O-methyl-glucuronic acid, mannose, xylose, arabinose, or galactose [26]. The composition of the hemicellulose is

dependent on the plant species that produced it [26], [27]. Compared to cellulose, hemicellulose is significantly easier to hydrolyze into small carbohydrate chains and monosaccharides. Currently, there are a number of methods for hemicellulose extraction and degradation, including steam explosion, dilute acid treatment, and ammonia explosion [9].

Lignin is the third kind of structural biopolymer, which composes 15-30% lignocellulosic biomass by weight [28]. In the structure of the cell wall, lignin fills the space between cellulose/hemicellulose fibers in plant cell walls. Unlike cellulose and hemicellulose lignin is not made from carbohydrates, but from phenylpropane units that are linked through enzymatic radical polymerization [29]. The monomers that plants employ to create lignin are cinnaminyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol. These monomers are bonded together through a number of different linkages that form a complex, amorphous structure. The most common of these bonds are the β-O-4, 5-5, β-5, β-1, and α-O-4 linkages (Figure 1.2), which represent 45-50, 18-25, 9-12, 7-10, and 6-8% of the linkages in softwood lignin, respectively [30]. Lignin is a major inhibitor of biological degradation of lignocellulose, as there are only a few species in nature that can effectively metabolize it [31], [32]. This recalcitrance, while beneficial for living plants, presents a significant challenge in the successful utilization of biomass in the production of fuels or other chemicals.

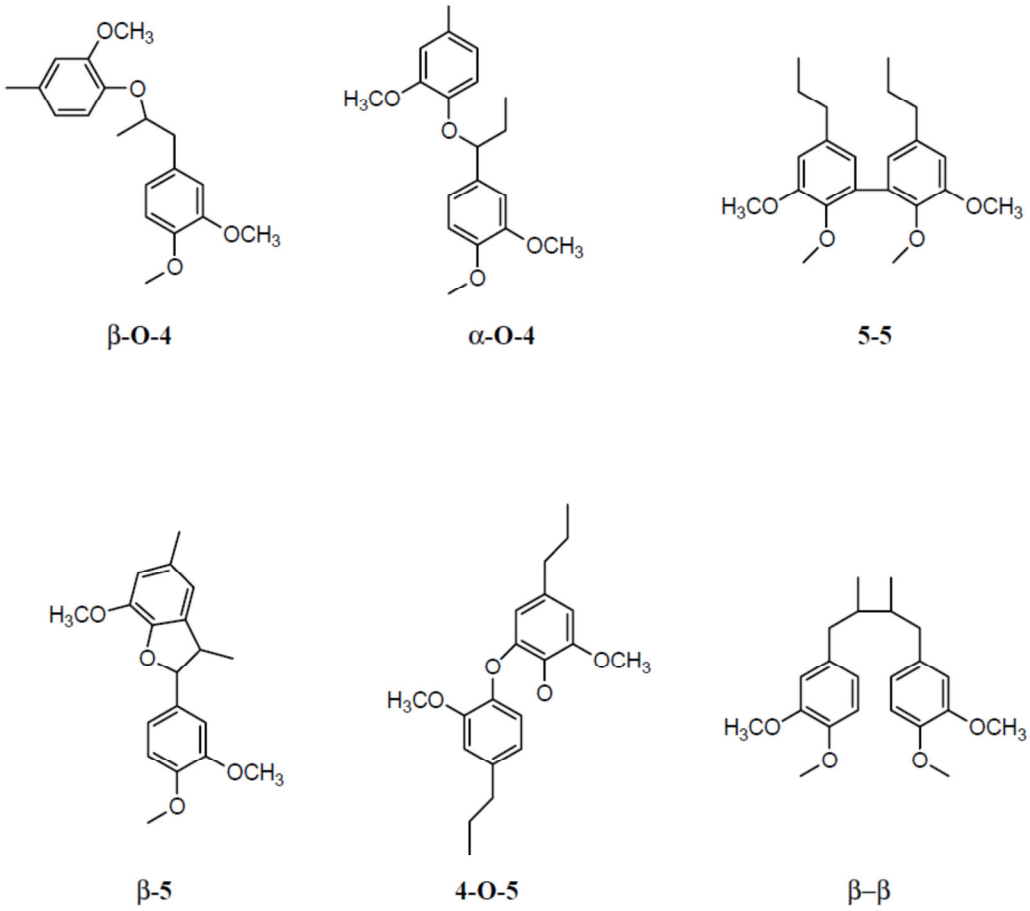

Figure 1.2: Common linkages in softwood lignin [30].

Currently, lignin is dealt with in biomass processing through a number of different techniques. The pulp and paper industry generally uses a process called kraft pulping, in which a strong bases and sulfur compounds are used to depolymerize and extract lignin from wood pulp [30], [33]. Other methods, such as acid pulping, organosolve pulping, and high temperature ethanol/water have been used to degrade lignin [34–38]. In other cases, biomass pretreatment has been used to access the polysaccharides through disruption of the biomass structure [9], [14].

Other sources of biomass can be used as substrates. Starches and simple sugars are currently used in the production of fuel ethanol. These carbohydrates can be sourced from corn, sugar cane, beets, or as a product from the depolymerization of longer chain polysaccharides [20], [39]. Algae have also received significant attention as a source of renewable oil cellulosic feed stocks [15]. In research on biomass catalysis, simple sugars are often used as a model or substitute for more complicated carbohydrates and biomass in general. Other sources of biomass may be similar to common lignocellulose, but have unique characteristics that warrant special attention. Rice hulls, for example, are coated in a layer of silica that makes effective catalytic conversion difficult [40].

1.1.2 Ionic Liquids

Ionic liquids were reported as early as 1914 when ethylammonium nitrate was shown to melt at 12°C [41]. In recent years the study of these compounds has experienced a resurgence. An ionic liquid is defined as a chemical compound that exists as an organic anion and a cation and has a melting point below 100°C. There are many different kinds of ILs, and many more are being developed (Figure 1.3). The most common forms are based on dialkylimidazolium, tetraalkylammonium, alkylpyridinium, or tetraalkylphosphonium cations coupled with an inorganic anion [42]. Due to their ionic character, ILs have essentially no vapor pressure. While it has been reported that some ILs can be distilled under the right conditions [43], in general, the vapor pressure is low enough to be neglected. Because ILs are composed of discrete anions and cations, the solvent properties, such as viscosity, melting point, and miscibility with other

solvents can be tuned through the right combination and design of each ion. The ability to design ILs to specific substrates, chemistries, and situations is important, because ILs are increasingly being looked to as a medium for applications, including biomass processing [44].

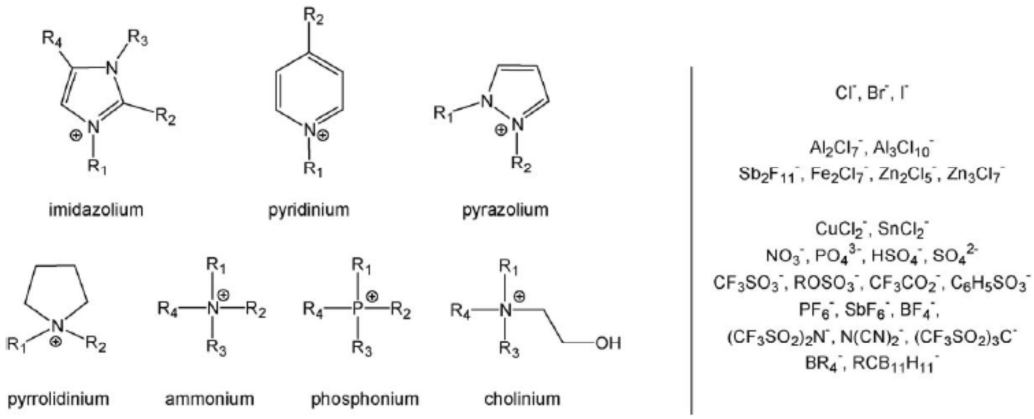

Figure 1.3: Anions and cations of some ILs described in the literature [45].

Additionally, most ILs display good stability under a wide range of chemical, thermal, and electrochemical conditions. Some ILs have reported thermal stability of over 300°C, although the stability is highly dependent on the identity of the IL's constituent ions [46]. There has been research to show that the long term thermal stability of some ILs is significantly less than that indicated by standard thermogravimetric analysis techniques [47]. This may be important in the development of biomass processing techniques in ILs, because one of the main advantages of ILs is the potential for the essentially complete recycling of solvents. ILs are also generally assumed to have good chemical stability. In many cases, strongly acidic, reducing, or oxidizing agents can be used without degradation of the ILs [48], [49]. There are,

however, some exceptions to this rule [50]. Dialkylimidazolium based ILs have a mildly acidic hydrogen that undergoes hydrogen exchange in aqueous media and can even deprotonate to form a reactive carbene under basic conditions [50], [51]. Some ILs, such as halide, acetate, or formate based ILs, can form volatile acids (such as hydrochloric, acetic, or formic acid) [43], [52]. Additionally, some ILs can be designed to be reactive with the addition of acidic moieties or metal centers [48], [53], [54]. ILs have also been looked to as media for novel electrochemistry, as some of them have a wide window of electrochemical stability [55].

ILs have found a place in a number of catalytic reactions. In many cases, the solvent properties of ILs increase reaction rate and selectivity [56–58]. Additionally, post reaction separations are often made easier due to immiscibility of products with the IL phase, such as in the case of esterification in acid ILs [59], [60]. ILs also give the ability to distill volatile products and reuse the IL [61]. The coordination of ILs to metal centers has also been shown to increase the activity and recyclability of some metal catalysts [49], [53]. While ILs are often designed around specific solvent properties, some ILs are designed to work as a combined solvent and catalyst. A common method for this is to attached an acid group to the end of an alkyl chain on the cation, which has been used to depolymerize cellulose and to catalyze esterification reactions [54], [62], [63].

Recently, some ILs have been shown to be able to either partially or completely dissolve cellulose, lignin, or lignocellulosic biomass. Imidazolium based ILs seem to be especially well suited for this application. The most common solvents that are used to dissolve biomass are alkylimidazolium chlorides, acetates, and formates, although others

have been investigated and used in biomass chemistry [21], [64], [65]. This property of ILs has been exploited in the production of novel materials, such as cellulosic aerogels and films in addition to being used as a solvent for catalysis of lignocellulose [66–68].

The property of these ILs that enable them to effectively dissolve biomass is their ability to function as a hydrogen bond acceptor while only having a limited ability to act as a hydrogen bond donor. In general, it is the ability of the anion form hydrogen bonds with the hydroxyl groups of the cellulose, disrupting the hydrogen bond crosslinking of the polysaccharide, that makes these ILs effective at solubilizing biomass [25], [69]. Dissolution of glucose in 1,3-dimethylimidazolium chloride was studied through computer modeling to analyze the IL/saccharide interactions further. This work demonstrated the almost exclusive coordination of the chloride anion to saccharides with only minimal contributions from hydrogen bonding and van der Waal forces from the imidazolium cation [70]. The dissolution process first swells the cellulose and, in the case of lignocellulose, extracts the lignin [71]. Some ILs have even been specifically designed to dissolve carbohydrates without denaturing enzymes to allow for homogenous enzymatic catalysis of biomass [72]. Some work has been done to investigate ILs using solvatochromic dyes to probe the hydrogen bonding acidity and basicity, the polarity, and dispersion forces in various ILs [73].

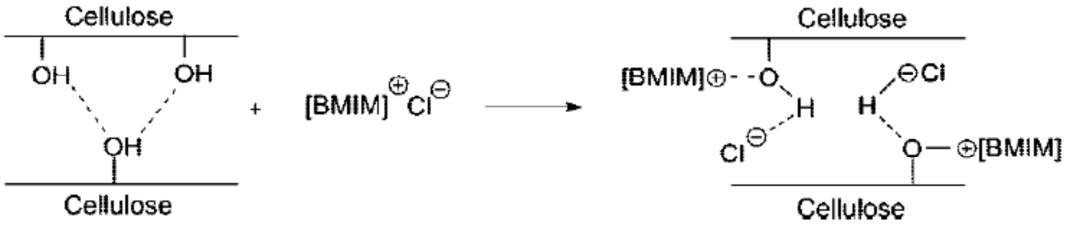

Figure 1.4: Proposed dissolution mechanism of cellulose in 1-butyl-3-methylimidazolium chloride (BMIMCl) [25].

1.2 CARBOHYDRATE CATALYSIS

1.2.1 Pretreatment of biomass

The production of ethanol through fermentation is already a common process for the utilization of biomass resources [39]. While simple sugars and starches can be easily used in this process, feed stocks of cellulose and hemicellulose would provide a source of sugars that would not compete with food and could be produced in otherwise unused land area. The conversion of these polysaccharides into simple sugars adds a significant challenge compared to the use of corn or sugarcane feed stocks [20]. In order for cellulosic biomass to be used in ethanol production, the feedstock must be pretreated and saccharified to provide a substrate suitable to the ethanol producing yeast. Pretreatment is a key step in a number of catalytic biomass processes [9], so while the pretreatment step itself may not be catalytic, it is important to an understanding of processing of biomass in ILs.

Because the structure of biomass, especially the presence of lignin, inhibits the saccharification of structural carbohydrates, pretreatment is needed to open up the

structure of plant matter (Figure 1.5). While a number of methods, such as steam explosion, dilute acid treatment, ammonia explosion, and milling have been explored, the unique solvent properties of ILs have garnered significant attention as a pretreatment option [9], [74]. What makes ILs promising for the catalytic treatment of biomass, namely their ability to make homogeneous solutions of lignocellulose, is also what make ILs a good medium for pretreatment. Because much of the recalcitrance of biomass to saccharification comes from the structure of the cell wall and the presence of lignin, when the structure is disrupted through dissolution in ILs, the carbohydrates are made available for enzymatic attack [71].

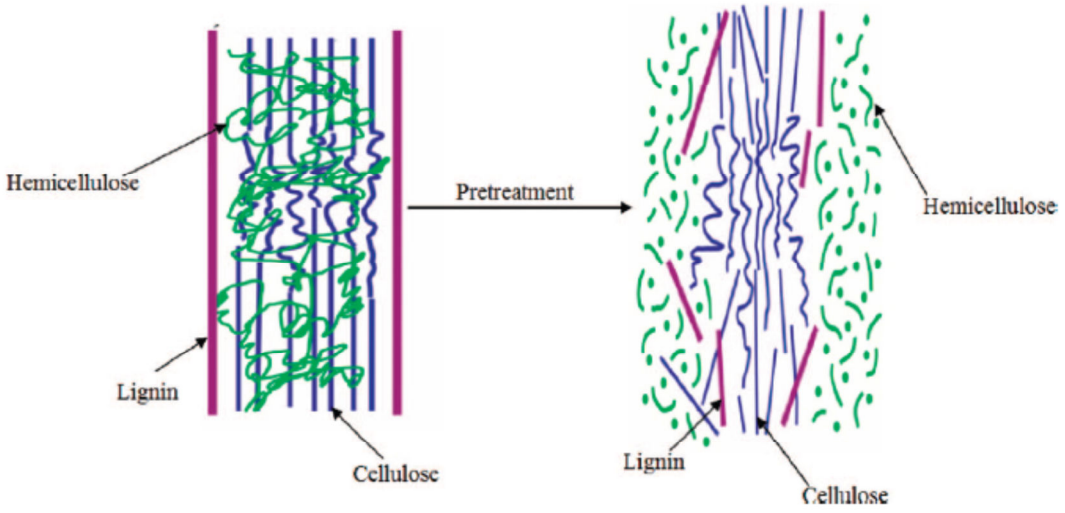

Figure 1.5: Schematic of the role of pretreatment in the conversion of biomass to fuel [74].

The general procedure for IL pretreatment of biomass is to dissolve or swell the biomass with an IL solvent. After treatment at a given temperature for a given time, an antisolvent, such as water, ethanol, or an acetone/water mixture, is added to precipitate

the biomass and wash away the IL (see Figure 1.6). The biomass is then dried and saccharified through enzymatic or chemical methods. This process builds off of the work by Rogers in which lignocellulose was fractionated into a cellulose and a lignin rich phase through dissolution in 1-ethyl-3-methylimidazolium acetate (EMIMAc). In this work, an acetone/water solution was added to precipitate the cellulose while keeping the lignin in solution. Simply evaporation of the acetone precipitates the lignin after the cellulose had been filtered from the solution [75].

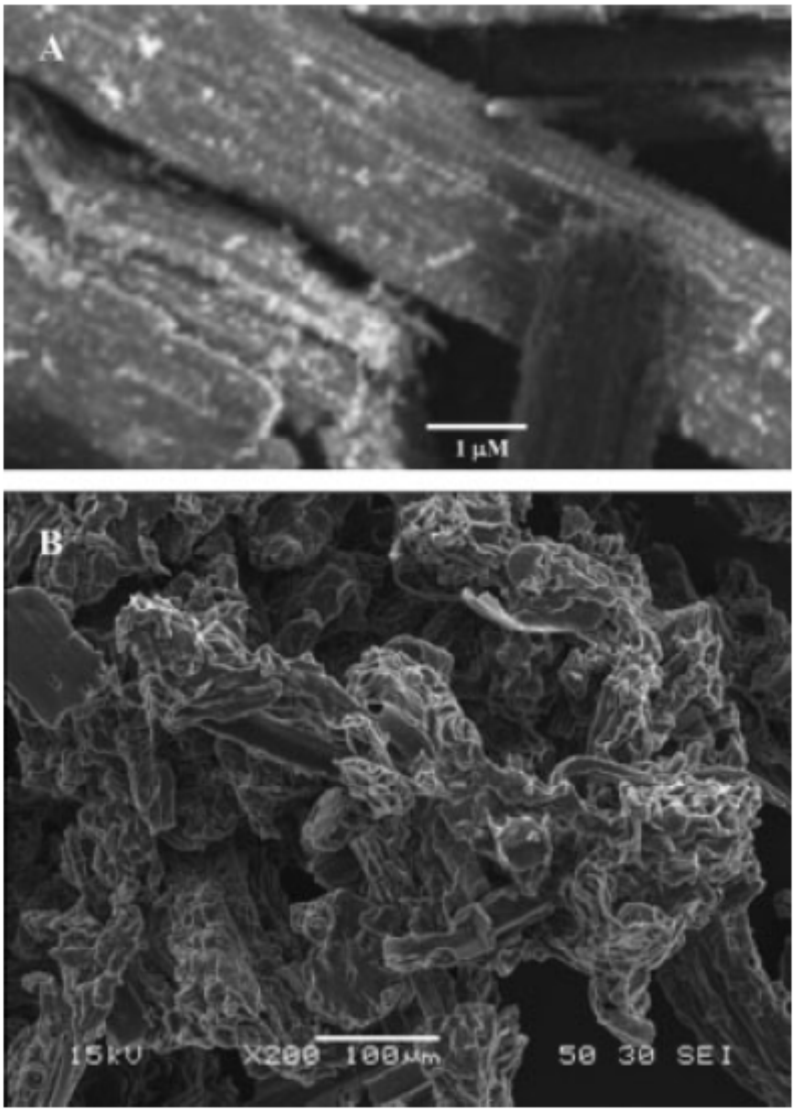

Figure 1.6: SEM micrographs of (a) untreated and (b) ionic liquid pretreated and recovered fibers from switchgrass [71].

This method was applied to pretreatment using a number of different ILs by a number of different researchers. Lynam conducted a study to measure the effect of a few different ILs on the composition and structure of lignocellulose in which ground rice hulls pretreated with 1-ethyl-3-methylimidazolium acetate, 1-allyl-3-methylimidazolium

chloride (AMIMCl), or 1-hexyl-3-methylimidazolium chloride (HMIMCl) and either ethanol or water as antisolvents for cellulose precipitation. In this study, the EMIMAc was able to completely remove the lignin and significant amounts of hemicellulose from the rice hulls, while the other ILs removed less lignin, but more hemicellulose [76]. Lee, et al. worked with EMIMAc and other ILs to treat wood flour for enzymatic saccharification. By removing the lignin and reducing the cellulose crystallinity, the IL treated wood flour was 95% digestible to cellulase enzymes from *Trichoderma viride* [77]. It has been demonstrated that this process works even at a biomass loading well above the solubility limit in the IL is effective at pretreatment [78]. The use of ILs as a pretreatment strategy has been compared to a more common method, namely pretreatment with dilute acid. In this study, it was found that IL pretreated samples produced a higher yield of monosaccharides and in a shorter time than samples pretreated with dilute acid [14]. Other ILs, such as 1-ethyl-3-methylimidazolium diethyl phosphate, alkyloxyalkyl substituted imidazolium acetate, or alkyloxyalkyl substituted ammonium acetate have also been investigated [79], [80]. Some studies have used variations on dissolution and washing, such as the addition of an ammonia treatment step [81] or a combining the pretreatment and saccharification into one step with aqueous ILs and enzymes [79].

One of the more difficult problems facing pretreatment of biomass with ILs or saccharification in ILs is the separation of the ILs and carbohydrates after the treatment is completed. Ideally, the products will be insoluble in the IL or be precipitated with an antisolvent. These options may not be sufficient, such as when monosaccharides must be

extracted from the IL. Brennan and coworkers developed a liquid-liquid extraction procedure for the removal of sugars from and IL phase using organic soluble boronic acids that have an affinity for sugars [82]. Another method relies on the use of kosmotropic, or water-structuring, salts to induce a biphasic system with water and an IL [83]. This effect has been used to separate and reuse ILs after pretreatment of biomass [84].

1.2.2 Hydrolysis of carbohydrates with acids

Cellulase enzymes are not the only catalysts that are effective for the saccharification of polysaccharides. In a number of reaction schemes for the utilization of biomass, lignocellulose must be hydrolyzed into monosaccharides. This is important not just in fermentation of biomass into ethanol, but also if the saccharides are to undergo processing directly into commodity chemicals or fuels. Without the use of ILs, the most common methods to hydrolyze polysaccharides into monosaccharides is through enzymatic hydrolysis or acid catalyzed hydrolysis [19]. This process can be slow and expensive, in part due to the necessity of heterogeneous reactions due to the insolubility of cellulose in conventional solvents. The ability of ILs to solubilize biomass has led to a considerable research effort in the hydrolysis of cellulose. These studies have focused on a wide range of catalyst, from conventional acid catalyst, both solid and homogeneous, to novel metal catalyst and ILs that are designed to be both solvent and catalyst.

Acid hydrolysis of lignocellulose is well understood and has been used to quantitatively saccharify biomass for decades [23], [85]. Because many ILs are stable

under acidic conditions, coupling the saccharification ability of acids with the dissolution ability of ILs is a natural choice. The acidity in any IL can only be as high as the conjugate acid of the anion of the IL. If HCl is added to an acetate based ILs, for example, acetic acid will be formed and the acetate anion from the IL will be effectively replaced by a chloride anion. The pH scale is not an appropriate measure of the acidity of an IL, as pH is defined in dilute aqueous solutions. For this reason, the Hammett acidity, as measured by nitroanilines of with known pKa values, is used to determine the acidity in ILs [86], [87].

A number of studies have been conducted in which biomass, acid, and an IL have been mixed to hydrolyze the polysaccharides into mono- or oligosaccharides. Proof of this concept was demonstrated by dissolving various cellulose sources, including spruce wood, in BMIMCl and adding HCl, sulfuric acid, nitric acid, or phosphoric acid with heat and stirring. With this method, glucose yields as high as 43% and total reducing sugars as high as 77% could be obtained after 9 hr [88]. Sievers et al. were able to depolymerize pure cellulose and the cellulose and hemicellulose in loblolly pine in 1-butyl-3-methylimidazolium chloride (BMIMCl) using 0.2 wt % trifluoroacetic acid as a catalyst. In the case of pure cellulose, 97% could be transformed into soluble mono- or oligosaccharides after two hours at 120°C, while 62% of the pine wood could be converted into soluble products (representing 97% of the carbohydrate content of the wood) [89]. Other experiments have been done with AMIMCl and added HCl to hydrolyze eucalyptus, pine, and spruce thermomechanical pulps. Higher HCl loadings

and longer reaction times resulted in higher degree of hydrolysis and yielding products consistent with lignin depolymerization [90].

A study by Li et al. demonstrated the hydrolysis of corn stalk, rice straw, pine wood, and sugarcane bagasse using combinations of the ILs 1-butyl-3-methylimidazolium bromide (BMIMBr), AMIMCl, 1-hexyl-3-methylimidazolium chloride (C_6MIMCl), 1-butyl-3-methylimidazolium hydrogensulfate (BMIMHSO$_4$), and 1-(4-sulfobutyl)-3-methylimidazolium hydrodrgensulfate (SBMIMHSO$_4$) with HCl, sulfuric acid, nitric acid, phosphoric acid, and maleic acid. BMIMCl coupled with HCl was found to be the most effective system. Interestingly, sulfuric acid was less effective than HCl, possibly due to interaction between the sulfuric acid and lignin [91]. While this study arrived at a similar conclusion as a few other works, it also worked with the naturally acidic ILs BMIMHSO$_4$ and SBMIMHSO$_4$. Other groups have worked with acidic ILs as catalysts in a number of situations [54], [59], [62]. Amarasekara et al. also utilized this novel kind of IL to depolymerize cellulose. In this work, it was found that 1-(1-propylsulfonic)-3-methylimidazolium chloride and 1-(1-butylsulfonic)-3-methylimidazolium chloride could dissolve cellulose up to a loading of 20g per 100g of IL at room temperature. The cellulose could then be hydrolyzed with the addition of water and mild heating (70°C) to produce up to 62% yield of reducing sugars and 14% yield of glucose [63].

Solid acid catalysts have also been successfully employed to hydrolyze the polysaccharides of biomass. A pair of studies by Rinaldi and coworkers demonstrates the ability of H-type ion exchange resins and zeolites to catalyze the depolymerization of

cellulose. This process showed continuously decreasing degree of polymerization of cellulose along with a continuously increasing yield of reducing sugars [92]. Further study examined the mechanisms of use of Amberlyst 15dry as an acid catalyst and determined the effects of catalyst concentration, substrate concentration, temperature, and impurities have on the reaction. Additionally, they found that the catalyst releases H^+ ions into solution, which subsequently catalyze cellulose depolymerization, instead of acting as a true heterogeneous catalyst [93]. Zhang and Zhao also studied H-form zeolites and H-type ion exchange resins in ILs as a method for depolymerizing cellulose but with the addition of microwave irradiation to effect the reaction. The combination of high surface area H-form zeolites and microwave irradiation produced a much quicker reaction, yielding 37% glucose after only 8 min [94]. When using solid catalysts, especially ion exchange resins, with ILs, it is important to note that ion exchange between the catalyst and IL. This makes the catalysis homogeneous and alters the composition of the IL.

1.2.3 Hydrolysis of carbohydrates with metal catalysts

Recently, Su et al. demonstrated the ability to use paired metal chlorides for the depolymerization of cellulose into monosaccharides and other products using paired metal chlorides. In this work, $CuCl_2$, $CrCl_2$, $CrCl_3$, $PdCl_2$, and $FeCl_3$ were initially tested as catalysts, but none were effective on their own. It was then discovered that by pairing $CuCl_2$ and $PdCl_2$, high yields of monosaccharides could be obtained. The total yield of products (including glucose, cellobiose, 5-hydroxymethylfurfural, and other) from this

reaction system was found to be as high as 70% with glucose yields up to roughly 45%. This yield is much higher and occurs much faster than when using sulfuric acid under the same conditions [95].

1.2.4 5-Hydroxymethylfurfural and other products

5-Hydroxymethylfurfural (HMF) can be produced from poly- and mono- hexoses and is a valuable platform chemical that can be used to make polymers, fuels, and commodity chemicals (Figure 1.7). HMF is the product of the dehydration of 6-carbon sugars such as fructose, glucose, and mannose. Because ketoses are furanoses when in their cyclic form, they are much easier to convert into HMF than aldoses. Polymers of six carbon sugars can also be used to produce HMF. The following procedure is generally used in the conventional production of HMF: 1) hydrolyze polyhexoses into monomers, 2) isomerize aldoses into ketoses, and 3) use an acid catalyst to dehydrate ketoses into HMF [96]. Once HMF is produced, it can be processed into fuels, resins, solvents, alkanes, fuel additives, or polymers as a replacement for petroleum recourses. The utility of HMF as a renewable biomass based platform chemical has led to significant research in the production of HMF in ILs, although the technology has still not matured into an industrial process [97], [98].

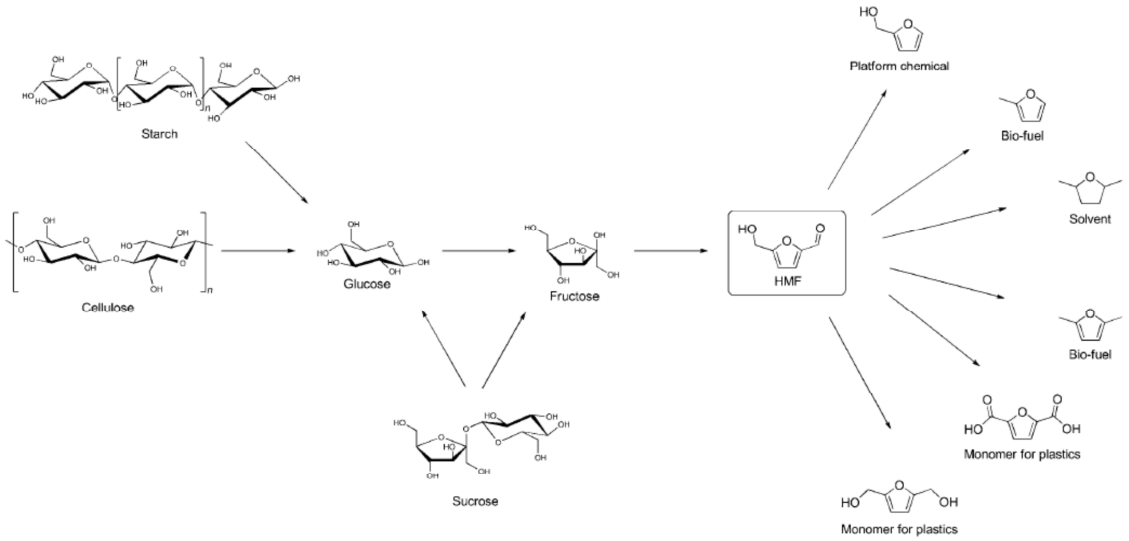

Figure 1.7: The synthesis of HMF from carbohydrates and its further derivatization to important chemicals [98].

Acid catalyzed dehydration of a ketose, such as fructose, is the easiest method for production of HMF. This method has been utilized successfully using ILs as solvents. Lansalot-Matras and Moreau demonstrated up to 80% yield of HMF from fructose in the ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) with added DMSO to solubilize fructose. The reaction in the IL phase worked much faster and produced a higher yield than the reaction carried out under the same conditions in pure DMSO [99]. Later, the same research group demonstrated the use of the acidic IL 1-H-3-methylimidazolium chloride as a combination solvent and catalyst by producing 92% yield of HMF from fructose and nearly quantitative amounts of HMF and glucose from sucrose. It was also noted in this article that there was no observed degradation of the HMF after the conclusion of the reaction [100]. Qi and coworkers tested sulfuric acid, HCl, phosphoric

acid, acetic acid, $CuCl_2$, $PdCl_2$, Dowex resin, and Amberlyst 15 as catalysts for production of HMF from fructose in BMIMCl. The Amberlyst catalyst was the best of the catalysts, producing an 83.3% yield of HMF after only 10 min [101]. Others have taken the idea of acid catalyzed dehydration of fructose in ILs and worked to make it more environmentally friendly by using ILs made from renewable materials. Hu et al. tested a number of ILs and found that choline chloride coupled with citric acid was the most effective system for the fructose to HMF conversion, achieving over 90% yield [102]. Acid catalyzed dehydration was tested on a number of different 6-carbon sugars by Sievers et al. through the use of added sulfuric acid in BMIMCl. Since glucose and mannose can both be isomerized into fructose, both sugars should be viable feed stocks for HMF production. As has been demonstrated previously, fructose gave high yields of HMF. Glucose only produced up to 12% HMF yield while only very small amounts of HMF were detected when mannose was used as a substrate. Additionally, xylose, a 5-carbon sugar, was shown to undergo an analogous reaction to form furfural with up to a 13% yield [103].

Recently, it was discovered that some metal chlorides can catalyze the conversion of aldoses such as glucose and mannose into HMF in ILs. Zhao et al. demonstrated the conversion of glucose to HMF using $CrCl_2$ in 1-ethyl-3-methylimidazolium chloride with a yield of almost 70%. Both $CrCl_2$ and $CrCl_3$ were found to be effective in this system, although $CrCl_2$ demonstrated the highest catalytic activity [104]. This discovery has led to many studies investigating metal chloride promoted production of HMF in ILs. Pidko et al. performed work using a combination of experimental techniques and computational

modeling to show that $CrCl_2$ and $CrCl_3$ effect the dehydration of glucose into HMF through ring opening and hydrogen shift catalyzed by $CrCl_4$ ions in solution [105], [106]. Binder et al. worked to elucidate the mechanism further through the use of glucose, mannose, galactose, lactose, tagatose, psicose and sorbose along with isotopic labeling. In this study, it was demonstrated that the chromium catalyst causes a 1,2-hydride shift which leads to a furanose that can be dehydrated [107]. In these studies, the efficacy of the $CrCl_2$/IL system could be enhanced through the use of microwave irradiation and by supporting the $CrCl_3$. The addition of microwave irradiation instead of simple heating in an oil bath allowed HMF to be recovered with up to a 40.2% yield after only 2.5 min while conventionally heated reactions obtained 32.5% yield after 32min [108]. In addition to $CrCl_2$ and $CrCl_3$, it has been shown that $SnCl_4$ can catalyze the dehydration of sugars, inulin, and starch into HMF in $EMIMBF_4$. In this system, and HMF yield of between 40 and 65% could be obtained, depending on substrate [109].

While production of HMF from monosaccharides is a useful technology, by producing HMF directly from lignocellulose, the saccharification step of biomass processing would be removed. Su et al. demonstrated the use of coupled metal chlorides to produce HMF from cellulose in a single step. By using $CuCl_2$ and $CrCl_2$ in EMIMCl, cellulose could be converted to HMF with a yield of 55.4% that stayed constant over several recycles of the IL/catalyst system. Additionally, the metal chlorides were shown to work in a synergistic manner, with almost no HMF production with either metal chloride on its own [110]. Binder and Raines demonstrated a similar system in which $CrCl_2$ or $CrCl_3$ in a solution of N,N-dimethylformamide (DMA) with LiCl and the IL

EMIMCl. With this system, fructose, glucose, cellulose and lignocellulose from corn stover and pine wood could all be converted into HMF. The yields were dependent on conditions and substrate, although even the lignocellulose produced up to a 48% yield [111]. By incorporating the use of microwave irradiation with the $CrCl_3$/IL system, glucose and cellulose could be converted to HMF with 90 and 60% yields, respectively [112]. Expanding the use of microwave treatments, lignocellulose from corn stover, rice straw and pine wood could be converted to HMF and furfural with yields of 45-52% and 23-31%, respectively with $CrCl_3$ in BMIMCl in 3 min or less [113].

1.2.5 Pyrolysis and deoxygenate production in ILs

There has been some research into deoxygenation and pyrolysis of carbohydrates in ILs. Generally, the thermal stability of ILs is prohibitively low to allow their use under the conditions needed for deoxygenation catalysts and pyrolysis. In some cases, however, ILs have been shown to support these reactions. Sheldrake et al. demonstrated the use of dicationic ILs as a medium for pyrolysis of cellulose to dehydration products of glucose. The ILs used were composed of two imidazolium rings connected with a 4-, 6-, or 9- carbon alkyl chain. Generally, pyrolysis occurs at temperatures above 300°C, but the use of these dicationic ILs allowed the productions of levoglucosenone, 1-(2-furanyl)-2-hydroxyethanone, and HMF along with trace amounts of levoglucosan at 180°C. Only 5.5% combined yield was obtainable for these products. Monocationic imidazolium ILs and dicationic pyridinium ILs were not thermally stable at this temperature and no products, other than IL decomposition products were detected [61].

Chidambaram and coworkers demonstrated the production of HMF and subsequent deoxygenation into 2,5-dimethylfuran in EMIMCl. While a number of acids were tested as catalysts, it was found that heteropoly acids gave a better combination of conversion and selectivity than any of the simple acids tested (such as sulfuric, fluoroacidic, nitric, HCl, and phosphoric). The best of the heteropoly acids, $H_3PMo_{12}O_{40}$ (12-MPA), produced a 71% conversion of glucose and a 89% HMF selectivity. To investigate the next step of processing HMF in ILs, metal catalyst were used to deoxygenate the HMF into 2,4-dimethylfurfural in the IL. Palladium, platinum, ruthenium, and rhodium catalysts supported by carbon were added to IL/HMF solutions at 120°C under 62 bar of H_2. The most effective of these catalysts was Pd/C which gave 19% conversion and 51% selectivity. When a small amount of acetonitrile was added to prevent the formation of humins, a conversion of 47% with 36% selectivity was obtained [114]. Other work has been done on the hydrodeoxygenation of lignin, as opposed to carbohydrates. This will be discussed later in this chapter.

1.2.6 Derivatization of biomass in ILs

Biopolymers are an important area of research as a replacement for petroleum derived products. In the US, 331 million barrels, or 4.6% of the total US petroleum consumption, were used to make polymers in 2006 (329 million as feedstock, 2 million for energy) [115]. By displacing the need for petroleum, production of biopolymers could lessen global oil demand. While cellulose, starches, and other naturally occurring biopolymers can be difficult to work with due to their chemical and physical properties,

chemical modification of these naturally occurring polymers (see Figure 1.8) allows for a wide range of properties to be achieved [116]. Additionally, modification of biopolymers can be used to aid in analytical methods by making otherwise insoluble polymers such as cellulose soluble in a wide range of solvents [117]. Smaller molecules of interest can also be manufactured through the chemical modification of monosaccharides. In many cases, it is even possible to couple the use of ILs and enzymes to effect a biocatalytic change while maintaining the advantages of an IL system [118]. Because ILs have the ability to solubilize unmodified biomass, they are well suited to the task of chemical modification of lignocellulose for a wide variety of applications. ILs are particularly well suited to chemical modification of carbohydrates because, generally, the sugars or biopolymers are more hydrophilic while the reactants for derivatization are more hydrophobic. The ILs are often able to solubilize both reactants and, in the case of smaller molecules, the amphiphilic product. Research into modification of biomass in ILs is also important because there is significant work focusing on using enzymes in IL based system, which could lead to other enzymatic processing of biomass in ILs.

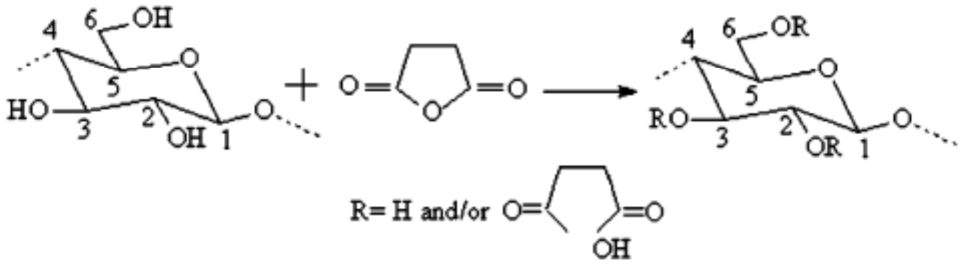

Figure 1.8: Reaction of cellulose with succinic anhydride [119].

The modification of monosaccharides with laurates is a common method for the production of surfactants. Glucose modification with vinyl laurates has been studied in ILs has been studied by Lee et al. in 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTfO) and 1-butyl-3-methylimidazolium bis(trifluorosulfonyl)imide (BMIMTf_2N). Using lipase enzymes, Lee and coworkers demonstrated that a super saturated solution of glucose in a mixture of BMIMTfO and BMIMTf_2N, along with ultrasound treatment produces a better conversion and yield in less time than subsaturation solutions in a pure IL without the ultrasound [120–122]. This reaction, producing sugar esters with lipase enzymes, has been demonstrated in other ILs, such as $BMIMBF_4$ and $BMIMPF_6$[123].

Modification of larger saccharide chains requires ILs that are better suited to biomass solvation. Unfortunately, the ILs that solvate cellulose and lignocellulose are also destructive to enzymes [124]. Consequently, most of the research in the modification of cellulose and lignocellulose uses non-enzymatic catalysts or no catalysts at all. Success has been seen in acetylation, carbanilation, sulfation, succinilation (Figure 1.8), and benzoylation of cellulose chains in imidazolium based chlorides and bromides along with choline chloride ILs [119], [125–128]. There has been work in combining the enzymes and ILs that will dissolve biomass. Zhao and coworkers developed ILs with $Me(EtO)_n$- substituted imidazolium and alkylammonium (where n=2-7) cations coupled with an acetate anion that are both effective for solubilizing cellulose and as a solvent for lipase catalyzed esterification. These ILs can dissolve cellulose up to 10 wt%, and support enzymatic esterification with methylmethacrylate with yield up to 66% [72].

1.3 LIGNIN CATALYSIS

While lignin catalysis in ILs has not received the same attention as cellulose and monosaccharides, there has still been some research in this area. The main goal of much of the research relating to lignin in ILs have been for the purpose of pretreatment [77], [81], [84], [129]. Sun et al. demonstrated the ability to fractionate wood into cellulose rich and lignin rich samples using EMIMAc and acetone/water as an antisolvent for cellulose followed by evaporation of acetone to precipitate the lignin [75]. Other groups then used this discovery as a stepping stone to pretreatment of biomass. While some use ILs as a path towards delignification for pretreatment [77], others have shown that a loss of cellulose crystallinity is also a source of IL pretreatment efficacy [14], [78], [80]. The other work in lignin catalysis has covered thermal and chemical depolymerization and hydrodeoxygenation. As lignin is a complex, amorphous polymer, most studies on lignin catalysis work with lignin model compounds as a way to test a process while keeping analytical complications to a minimum.

One of the simplest treatments of lignin in ILs is to simply dissolve lignin and heat for a period of time. Kubo et al. performed a series of experiments with the lignin model compound guaiacylglycerol-β-guaiacyl ether (GG) mixed with BMIMCl, EMIMAc, or AMIMCl at 120°C. This model compound simulates the β-O-4 ether linkage in lignin, which is the most common structure in lignin. The main product of this reaction was 3-(4-hydroxy-3methoxyphenyl)-2-(2-methoxyphenoxy)2-propenol, which is an enol ether (EE). EE is the dehydration product of GG, and an analogous process has been implicated as an intermediate in the depolymerization of lignin under both acidic

and alkaline conditions [130]. This intermediate has been detected in other studies involving lignin model compounds.

The cleavage of the β-O-4 ether linkage is a possible pathway both to general delignification of biomass and to the utilization of lignin as a feedstock for fuel and chemical production [131], [132]. A number of methods have been explored to sever this bond. In one study, N-bases were used in 1-butyl-2,3-dimethylimidazolium chloride (BDMIMCl). It was demonstrated that the base 1,3,5-triazabicyclo[4.4.0]dec-5-ene (TBD) was effective at cleaving the β-O-4 ether linkage in GG with a yield of up to 23%. As in the study by Kubo et al., EE was observed as in intermediate. Other N-bases, including 7-methyl-1,3,5-triazabicyclo[4.4.0]dec-5-ene (MTBD), did not show the same activity as TBD, indicating a unique functionality for TBD. It was suggested that TBD could act as a combination base and nucleophile to break down lignin using the same mechanism as kraft pulping, although the process was not shown to be catalytic [133]. The trialkylimidazolium IL was utilized in this study as opposed to the more common dialkylimidazolium ILs because the hydrogen at the 2 position on the dialkylimidazolium ring can be extracted under basic conditions to form a reactive carbene [50]. Another method, using metal chlorides as catalysts, was demonstrated to be effective at the hydrolysis of both phenolic and non-phenolic lignin model compounds. In this study, GG and veratrylglycerol-β-guaiacyl ether (VG) were used to model the β-O-4 ether linkage in lignin. $FeCl_3$, $CuCl_2$, and $AlCl_3$ were shown to be effective at catalyzing the hydrolysis of the ether linkage with $AlCl_3$ showing the highest yield of 80% for GG and

75% for VG. The metal chlorides most likely acted as acid catalysts to break the bond through the same mechanism of other acid promoted systems [134].

The task specific acidic IL HMIMCl has been shown to catalytically hydrolyze the ether bonds in both GG and VG up to a 71.5% yield. The mechanism for this hydrolysis starts with dehydration into an enol ether structure, which is then susceptible to acidic attack of the β-O-4 ether linkages. This process, as shown in Figure 1.9, occurs both in the individual model compounds and dimers of the model compound that form under reaction conditions [135]. This method was extended to a number of other acidic ILs. ILs composed of 1-H-methylimidazolium cations and chloride, bromide, hydrogensulfate, and tetrafluoroborate anions, along with $BMIMHSO_4$ were used to hydrolyze the β-O-4 ether linkage in GG and VG. HMIMCl was found to be the most effective of these ILs. The Hammett acidity of each of these ILs was measured using UV-Vis measurements to determine protonation of 3-nitroaniline added to the ILs, but the acidity of the IL did not correlate with the yield of hydrolysis products. The factor that determined the efficacy of acid catalyzed hydrolysis in these ILs was the ability of the anion to hydrogen bond with the hydroxyl groups on the lignin model compounds [86]. Further study demonstrated the ability of HMIMCl to depolymerize lignin through acid catalyzed hydrolysis of the β-O-4 ether linkage. The lignin used was extracted from oak wood using EMIMAc. Treated lignin was demonstrated to be reduced in size from the untreated lignin and the disappearance of the ether structures was observed through NMR and IR spectroscopy [132].

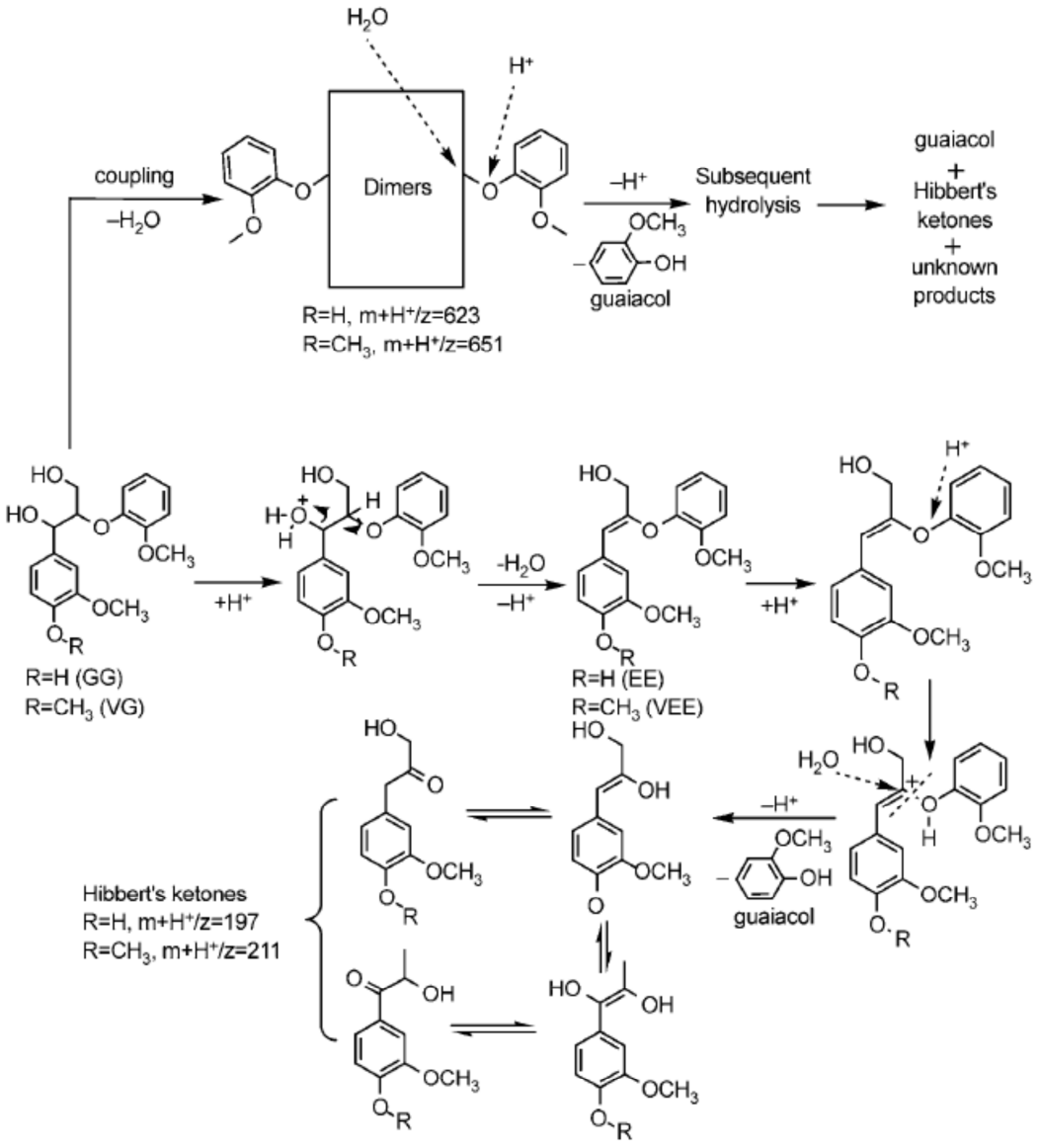

Figure 1.9: Proposed acid-catalyzed mechanism for hydrolysis of β-O-4 bonds in GG and VG [135].

Other transformations of lignin have been demonstrated in ILs as well. Binder et al. performed work with many catalysts in EMIMCl and 1-ethyl-3-methylimidazolium triflate (EMIMOTf). While a number of catalysts were able to dealkylate the lignin

model compound eugenol, these catalysts failed to produce monomeric products from organosolv lignin [136]. Further use of metals for lignin catalysis in ILs was demonstrated by Jiang and Ragauskas. This study dealt with the use of vanadyl acetylacetonate in $BMIMPF_6$ along with Cu(II) or Cu(I) co-catalysts to selectively oxidize aromatic alcohols into carbonyl or carboxylic acid groups. While most of this work focused on a wide variety of alcohols, a few compounds were specifically noted as being model compounds for lignin [137]. Other work has been performed with metal catalysts in ILs for the purpose of deoxygenation of lignin model compounds. In a study by Yan and coworkers, cyclohexanol was dehydrated into cyclohexene with Brønsted acidic ILs. Then, by combining the acidic ILs with Ru, Rh, or Pt nanoparticles, phenolic lignin model compounds were hydrogenated and deoxygenated to non-aromatic hexane species [138]. Other work on hydrodeoxygenation of lignin in ILs have been limited because temperature where traditional hydrodeoxygenation catalysts function is above the stability limit of IL, especially those that have the ability to solubilize biomass.

1.4 CONCLUSIONS

Researchers have been applying significant effort in the field of catalytic processing of biomass in ILs for roughly a decade. There is, however, much more work to be done and room to grow. While ILs have begun working their way into some pilot scale and industrial processes [45], the technology for IL use in biomass processing on an industrial scale may still be somewhat immature. Because there is such a wide range of possibilities with respect to IL selection and design, catalysts, and conditions, along with

a wide variety of processes and biomass sources to focus on, there is still much work to be done.

ILs present a unique set of challenges as well as a unique set of advantages as solvents for processing biomass. The advantages of lignocellulose solvation, enhanced catalyst activity, recyclability and, in some cases ease of separations make ILs a promising avenue of research and suggest a place in the next generation of biorefineries. In addition to the basic research needed to find the optimum combination of IL/catalyst/substrate, overcoming the unique challenges of ILs must be thoroughly investigated [139]. Because ILs are significantly more expensive than conventional solvent, efficient recycle is key to their utilization in any industrial setting. One of the most difficult challenges of working with biomass in ILs, especially in the case of simple carbohydrate production, is separating the products from the IL after the reaction is complete. As discussed, only a few studies have been performed in which monomeric carbohydrates are removed from ILs. Additionally, the ILs that tend to work well for processing of lignocellulose also tend to have lower thermal stability than other common ILs. When taking the work done with compounds such as monosaccharides and lignin model compounds and applying it lignocellulose, care must be taken to match ILs that will work for the process developed on the model system and accommodate the realities of a more difficult lignocellulosic substrate. Processes designed with ILs will need to take these challenges into account, along with possible health effects and corrosion caused by highly ionic media [140].

Even with the potential difficulties that ILs pose in developing new industrial processes, the promise of homogenous conversion of biomass into fuels, commodity chemicals, and polymers is a strong motivator. The potential for success is high. More research into processing of biomass in ILs to optimize recent discoveries, develop separations and recycling processes, and discover new uses for IL/biomass systems has the potential to move this field towards pilot scale and eventually to full scale production.

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Chapter 2: Objectives

The objectives of this work are to develop and understand methods for the depolymerization of lignin in ionic liquids as well as to apply these methods to biomass processing. Two of the most common methods of lignin depolymerization, base catalyzed and acid catalyzed depolymerization will be explored. Using these chemical processes, coupled with the concept of lignocellulose processing in ionic liquids, this work will attempt to depolymerize lignin through the hydrolysis of the β-O-4 ether linkage as well as investigate the unique aspects presented by ionic liquid systems. Because lignin is an ill-defined amorphous biopolymer, initial studies into lignin depolymerization in ionic liquids were conducted with lignin model compounds. Guaiacylglycerol-β-guaiacyl ether (GG) and veratrylglycerol-β-guaiacyl ether (VG) were used as phenolic and non-phenolic model compounds for this purpose. The cleavage of the β-O-4 ether linkage was easily tracked through the production of guaiacol from these model compounds.

The most common method for depolymerizing lignin is utilized mainly in the pulp and paper industry. In this method, called kraft pulping, a strong base is added to an aqueous slurry of wood pulp along with a sulfur based nucleophile. Chapter 3 presents work on a system that takes inspiration from kraft pulping by utilizing strong bases in ionic liquids to depolymerize lignin model compounds. The trialkylimidazolium based ionic liquid 1-butyl-2,3-dimethylimiazolium chloride was used because the more common dialkylimiazolium based ionic liquids can form reactive carbenes under strongly basic conditions. Multiple organic N-bases were utilized in this study because inorganic

bases were not soluble in the ionic liquids. Only one of these N-bases, 1,3,5-triazabicyclo[4.4.0]dec-5-ene (TBD), was shown to cleave the ether linkage of the model compounds to a significant degree. Based on the experimental results, it was proposed that TBD acted as both base and nucleophile to affect the cleavage of the β-O-4 ether linkage. This reaction was not found to be catalytic.

Chapter 4 will cover initial studies on acid catalyzed depolymerization of lignin in ionic liquids. For this study, the acidic ionic liquid 1-H-3-methylimidazolium chloride (HMIMCl) was chosen as a combination solvent and catalyst. Through a number of tests with GG and VG, it was demonstrated that HMIMCl was effective at catalytically hydrolyzing the β-O-4 ether linkage of the model compounds. The mechanism of this hydrolysis was tracked through identification and isolation of a few key intermediates. A dimer of the model compound and an enol ether (EE) that resulted from the dehydration of the model compound were the key intermediates in cleaving the ether bond. High yields of guaiacol, indicating ether hydrolysis, could be produced at various model compound loadings and after a number of recycles of the ionic liquid.

There are a number of different acidic ionic liquids that can be used for lignin depolymerization. HMIMCl is produced by neutralizing methylimidazole with HCl. If different acids are used, such as HBr, HBF_4, or H_2SO_4, acidic ionic liquids with different properties can be produced. As will be discussed in Chapter 5, acidic ionic liquids based on the 1-H-3-methylimidazolium cation with chloride, bromide, tetrafluoroborate, and hydrogen sulfate anion, along with 1-butyl-3-methylimidazolium hydrogen sulfate, were used to catalyze the hydrolysis of the β-O-4 ether linkage in GG and VG. Each of the

tested ionic liquids gave a different yield of hydrolysis products. To test whether the relative acidity of each ionic liquid was leading to the difference in reactivity, the Hammett acidity of each ionic liquid was measured using 3-nitroaniline as an indicator. While the acidity of the ionic liquids varied between 1.48 and 2.08, the relative acidity did not match the relative reactivity of the ionic liquids. It was determined that the ability of the acidic ionic liquid to catalyze the hydrolysis of the β-O-4 ether linkage was dependent on the hydrogen bond basicity of the anion. Stronger hydrogen bond accepters promoted the conversion of GG to the EE intermediate more effectively than weakly interacting anions.

In Chapter 6, the insight gained through the use of model compounds is used to depolymerize oak wood lignin in HMIMCl. The lignin was obtained through the dissolution of oak wood powder in 1-ethyl-3-methylimidazolium acetate, followed by the precipitation of cellulose with an acetone/water solution and filtration. When the acetone was evaporated, the lignin precipitate was filtered and used as a substrate for depolymerization research. Gel permeation chromatography was used to track the depolymerization of the lignin. The hydrolysis of the β-O-4 ether linkage through the mechanisms predicted by model compound studies was verified through FT-IR, NMR, and water free control experiments.

One of the applications for lignin depolymerization technology is the pretreatment of biomass for saccharification and fermentation. In Chapter 7, pretreatment of lignocellulosic biomass will be explored through the reactive delignification of pine wood in HMIMCl. By treating wood with an acidic IL for times of 5 hr or less at

temperatures between 110°C and 150°C, the lignin in the wood samples could be extracted and depolymerize in one step. Additionally, the acidic IL removed the hemicellulose from the wood samples. The recovered cellulose rich fractions were washed, dried, and saccharified with cellulase enzymes from *Trichoderma viridae* to demonstrate the efficacy of the pretreatment.

Chapter 8 is the concluding chapter for this work. This chapter will contain prospects for the research performed and biomass treatment in IL. Additionally, the possibility of further research in this area will be discussed.

Chapter 3: Decomposition of a lignin model compound with organic N-bases in an ionic liquid*

3.1 INTRODUCTION

Development of alternative energy and chemical feedstocks can relieve reliance on petroleum-based sources. Biomass, due to its abundant reserves, renewability and low cost, is looked to as one alternative. Lignin, accounting for 18-40 wt% of the dry wood, is the second most abundant biomass component [1]. Further, lignin with an amorphous aromatic structure, is a potential feedstock for aromatic chemical compounds. The basic subunits of lignin are phenylpropane monomers that link together primarily through the C-O bonds in α- and β-aryl alkyl ethers [2]. The β-O-4 linkage is the most common structure in the lignin macromolecule [3]. Due to its complex structure and resistance to degradation, lignin is generally burned (energetic utilization) in the course of recovery of chemicals in kraft pulping. Therefore, cleaving the β-O-4 linkage is an optional strategy for depolymerizing lignin if producing aromatic fine chemicals from lignin is desired.

Kraft pulping as the industrial method of lignin depolymerization works in the presence of NaOH, which promotes the formation of quinone methide and alkoxide anion (at the α-hydroxyl group) intermediates for phenolic and non-phenolic phenylpropane units, respectively. An extra nucleophile, such as HS^- or anthraquinone, is employed to attack the α-carbon of quinone methide, which eventually undergoes the cleavage of β-ether bond [2–4]. However, developing new methods to degrade lignin is necessary to preserve the aromatic character and maximize the production of carbohydrates.

* Significant portions of this chapter have been previously published as: S. Jia, B. J. Cox, X. Guo, Z. C. Zhang, and J. G. Ekerdt, "Decomposition of a phenolic lignin model compound over organic N-bases in an ionic liquid," *Holzforschung*, vol. 64, no. 5, pp. 577–580, Aug. 2010.

Minimizing repolymerization of degradation products is also an important issue in some systems [5].

Ionic liquids (ILs), consisting of anions and cations that are liquid at or near room temperature, have attracted much attention as a medium in biomass processing [6]. ILs have been shown to dissolve wood pulp, cellulose, and lignin [7–9]. Sugars and cellulose have been converted into 5-hydroxymethylfurfural in ILs, which illustrates a promising pathway for biomass conversion [10], [11]. Recently, an enol-ether (EE), 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol, was found in ILs as a primary decomposition product from guaiacylglycerol-β-guaiacyl ether (GG), which features the β-O-4 ether linkage [12]. However, EE is essentially a dehydration product. The dealkylation of lignin model compounds has also been studied in ILs with H_2, in which 11.6% yield of the dealkylation product was obtained [13]. The dealkylation of lignin is more difficult than cleaving the C-O bonds, however.

The objective of this work was to explore the feasibility of breaking down the β-O-4 ether linkages in lignin by means of organic bases in ILs. GG was employed as a model reagent for lignin since it features a phenolic β-aryl ether bond (Figure 3.2). A series of organic N-bases – such as TBD, MTBD, DBU, TMG, and DABCO (Table 3.1 and Figure 3.1) – exhibited good solubility in imidazolium-based ILs and were tested.

N-base	Abbrev.	*pKa*	Reference
1,5,7-triazabicyclo[4.4.0]dec-5-ene	TBD	25.9	Schuchardt et al. (1998)
7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene	MTBD	25.43	as above
1,8-diazabicyclo[5.4.0]undec-7-ene	DBU	24.32	as above
1,1,3,3-tetramethylguanidine	TMG	23.3	as above
1,4-diazabicyclo[2.2.2]octane	DABCO	18.29	Streitwieser and Kim (2000)

Table 3.1: The *pKa* of different N-bases in acetonitrile.

3.2 EXPERIMENTAL

Guaiacylglycerol-β-guaiacyl ether (GG 99%, Figure 3.2), DABCO (98%), and 3,4,5-trimethoxybenzaldehyde (98%) were purchased from Tokyo Chemical Industry Co. Ltd. DBU (98%) was purchased from Acros Organics. 1-Butyl-2,3-dimethylimidazolium chloride ([BDMIm]Cl 97%, Figure 3.1) and the bases shown in Table 3.1 – TBD (98%), MTBD (98%), TMG (99%) –, guaiacol (98%), coniferyl alcohol (98%) and 4-(1-hydroxyethyl)-2-methoxyphenol (97%) were purchased from Sigma-Aldrich. Veratrylglycerol-β-guaiacyl ether (VG 97%) was purchased from Astatech, Inc. All the chemicals were not purified before the experiments unless otherwise noted.

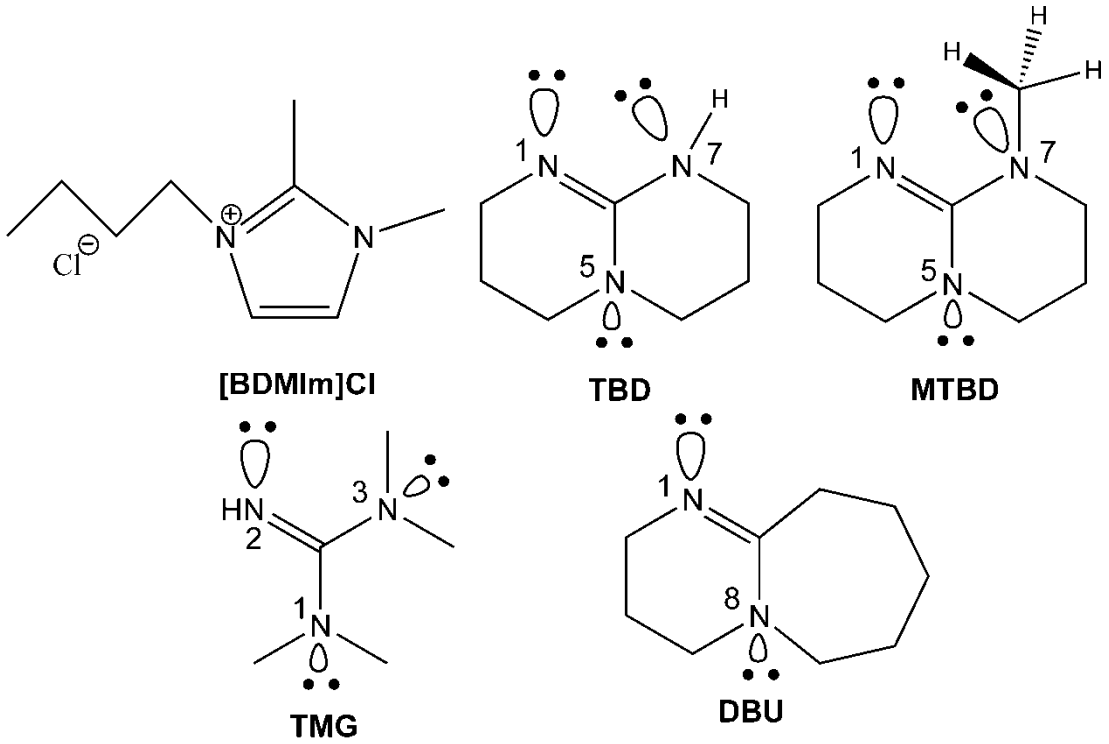

Figure 3.1: Structures of [BDMIm]Cl, TBD, MTBD, TMG and DBU.

In a standard experiment, [BDMIm]Cl was vacuum dried before use. 0.025 mmol N-bases were loaded into the vials (0.3 ml) with 100 mg [BDMIm]Cl and a magnetic stir bar. Reaction condition in a Reacti-Therm heating and stirring module (Thermo Scientific): The vials were sealed and stirred at 300 rpm for 5 min at 130°C. Then 0.025 mmol GG were added into the vials and the vials were stirred at 300 rpm for 2 h at 130°C. After the reaction cycle, 100 µl water was put into each vial after the vials were cooled down in ice water. 50 µl acetic acid aqueous solution (1:1 to N-base by mol) was added into each vial. Then the solution was added into 2 ml H_2O-acetonitrile (1:9 by volume). The diluted solution was analyzed by HPLC.

HPLC: Dionex Ultimate 3000 series with a UV detector (at 280 nm) and a Phenomenex Gemini C6-phenyl column (4.6×50 mm, 3 μm). Mobile phase: Mixed H_2O-acetonitrile. 3,4,5-Trimethoxybenzaldehyde was added as the internal standard for the quantitative calculations.

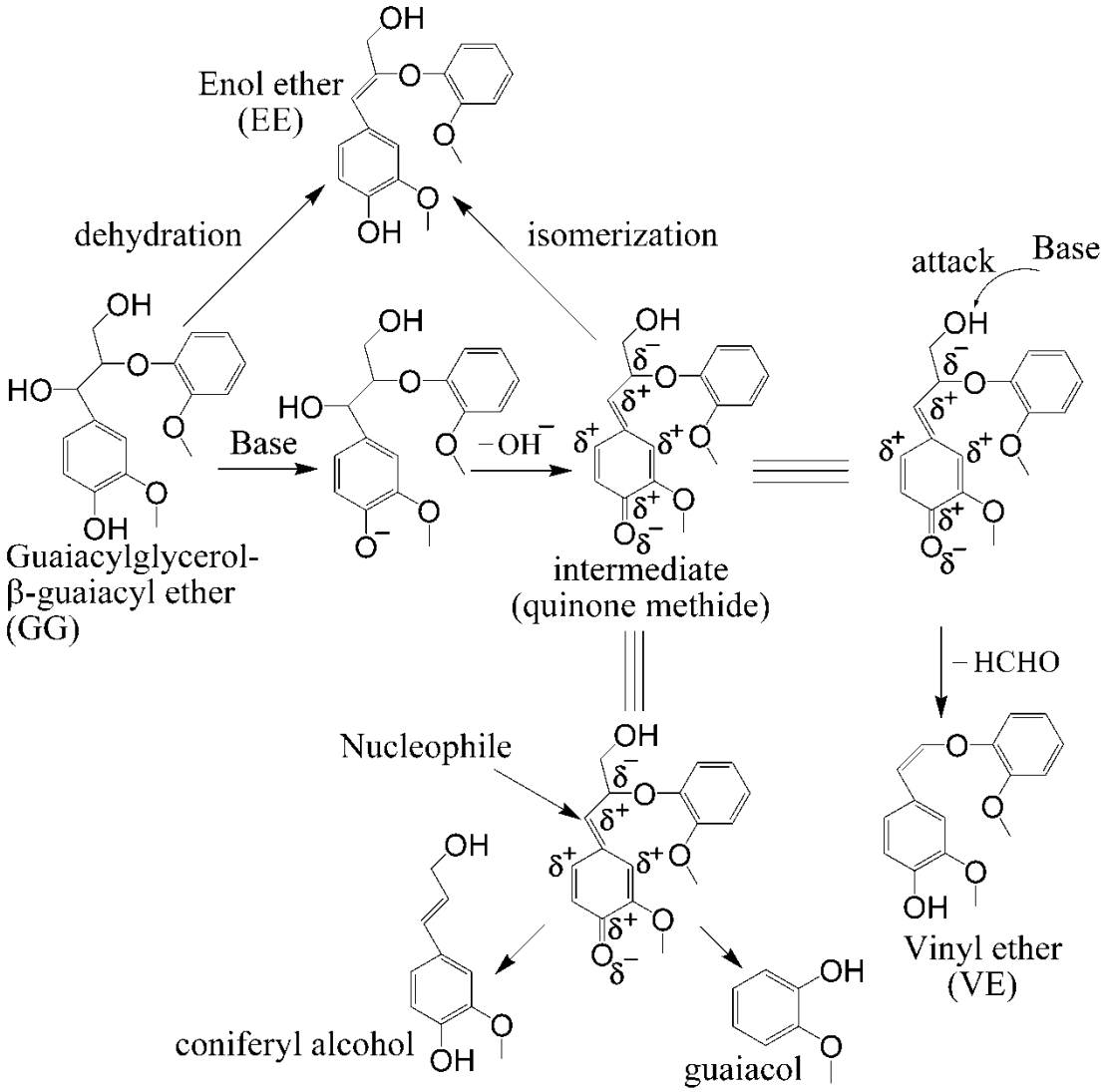

Figure 3.2: Possible reaction pathways on the conversion of GG into the primary products

Liquid chromatography-mass spectroscopy (LC-MS): Thermo Scientific LTQ-XL series system coupled to a thermo surveyor HPLC system with the same column and mobile phase as indicated above. NMR: Varian INOVA 500MHz series system.

NMR of 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol (EE)

^{1}H-NMR ($CDCl_3$-TMS at 25°C):δ 3.705 (3H, s, CH_3O-A3), 3.878 (3H, s, CH_3O-B2), 4.132 (2H, s, H-Cγ), 6.057 (1H, s, H-Cα), 6.784 (1H, d, J = 8.3 Hz, H-A5), 6.817 (1H, m, H-B5), 6.935 (1H, dd, J = 5.1, 1.5 Hz, H-B3), 6.951 (1H, dd, J = 5.1, 1.5 Hz, H-B6), 6.984 (1H, m, H-A6), 7.001 (1H, m, H-B4), 7.275 (1H, d, J = 2.0 Hz, H-A2). ^{13}C-NMR ($CDCl_3$-TMS at 25°C) δ 55.543 (CH_3O-A3), 55.983 (CH_3O-B2), 62.481 (Cγ), 110.954 (C-A2), 112.448 (C-B3), 114.097 (C-A5), 115.005 (Cα), 117.613 (C-B6), 121.239 (C-B5), 122.587 (C-A6), 123.715 (C-B4), 126.660 (C-A1), 144.241 (C-B1), 144.937 (C-A4), 146.182 (C-A3), 149.611 (Cβ), 150.072 (C-B2).

3.3 RESULTS AND DISCUSSION

[BDMIm]Cl was used as a typical solvent for this work due to the reported instability of most common dialkylsubstituted imidazolium-based ILs under basic conditions [14], [15]. Guaiacol, coniferyl alcohol, [E] / [Z] EE isomers, and a pair of vinyl ether isomers (VE), (1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethene), were the primary products detected by HPLC and LC-MS. However, VE is not very stable as reported by Kuroda et al. (2007), so we do not list VE yield.

The effect of different bases on the GG conversion and product yields are listed in Table 3.2. In the absence of a base, only a low GG conversion and EE isomers with a very low yield were observed at 130°C. This result is consistent with published work showing the dehydration product EE from GG with a low yield in the ILs with a chloride anion at 120°C [12]. When TMG, DBU or MTBD was added, increased GG conversion and EE yield were obtained as well as some guaiacol and coniferyl alcohol. When TBD was added, GG conversion and EE yield were the highest among all the tested N-bases, and, interestingly, a guaiacol yield of 23.0% was observed. The results show that TBD functions differently in the activation of GG and the cleavage of the β-O-4 bond. Higher temperature (Entry 8) enhanced the GG conversion and guaiacol yield over TBD. The cleavage reaction of the β-O-4 bond appears to be non-catalytic over TBD. In additional studies with TBD (not shown) for longer times and with lower TBD to GG ratios at 130 and 150°C, the absolute yield of guaiacol never exceeded the amount of TBD added.

Entry	N-base	GG Conv. (%)	Product yield (%)		
			Guaia-col	Coniferyl alcohol	[Z] EE[d]
1[a]	None	3.1	0.0	0.0	2.8
2[a]	TBD	66.9	23.0	3.0	24.5
3[b]	TBD	41.7	8.0	0.6	12.7
4[a]	MTBD	36.6	2.8	1.9	20.0
5[a]	DBU	31.2	2.0	1.8	18.7
6[a]	TMG	11.1	1.0	0.8	7.2
7[a]	DABCO	2.4	0.0	0.0	1.8
8[c]	TBD	94.3	42.3	6.5	25.0

[a] 0.025 mmol GG was added into the reaction vials with 100 mg [BDMIm]Cl and 0.025 mmol N-bases and heated at 130°C for 2 h.
[b] The same as (a) except 10 μl (0.56 mmol) water was added into the reaction vial.
[c] The same as (a) except the reaction vial was heated at 150°C.
[d] Stereoselectivety of [Z] over all the EE isomers was higher than 95%, so only [Z] EE is reported.

Table 3.2: Results for the reactions of GG over different N-bases

Control experiments verify that guaiacol is produced by the cleavage of the β-O-4 bond. 4-(1-Hydroxyethyl)-2-methoxyphenol (0.025 mmol) was added into a reaction vial with 100 mg [BDMIm]Cl and 0.025 mmol TBD and heated for 2 h at 130°C. No guaiacol was detected, which implies that guaiacol was not produced by cleavage of the C-C bond between the benzene ring and α-carbon but through the β-O-4 bond. The stabilities of guaiacol and coniferyl alcohol were also tested under reaction conditions. These compounds were added (0.0089 mmol each) to a reaction vial with 100 mg [BDMIm]Cl and 0.025 mmol TBD and heated for 2 h at 130°C. The recovery of guaiacol and coniferyl alcohol was 91.2% and 26.7%, respectively, which explains why the coniferyl

alcohol and guaiacol yields differ over TBD. This also implies that low guaiacol yields over the other N-bases are not associated with subsequent guaiacol reaction.

Figure 3.2 presents the possible reaction paths from GG to the primary products, EE, VE, guaiacol and coniferyl alchohol. Base-promoted formation of quinone methide is a key intermediate reaction for phenolic β-aryl (and α-aryl) ethers, leading to the conversion of GG (and phenolic lignin units) [2]. With GG the quinone methide should lead to VE and guaiacol. When VG, a non-phenolic lignin model compound that cannot form the quinine methide intermediate, was subjected to the same conditions as GG indicated in Table 3.2, entry 2, VG conversion was 5.0% and guaiacol yield was 2.2%. We suggest an additional pathway beyond GG dehydration that is functional under the conditions employed in Table 3.2 to EE and that involves the isomerization of quinone methide. In the absence of a base, we only observed a low EE yield. Adding the N-bases increased the GG conversion and EE yield. Amidines and guanidines are important agents in the deprotonation reactions of weak O-H, N-H and C-H bonds [16], and deprotonation is the first step in quinone methide formation from GG. If the N-bases led to quinone methide formation via this pathway, one would expect lower GG conversion with decreasing base strength. Table 3.1 compares the basicity and documents the decreases in GG conversion as a function of the *pKa*. DABCO, the weakest base tested, exhibited virtually no reactivity, presumably because it was not strong enough to withdraw the phenolic hydrogen of GG to produce quinone methide.

The quinone methide intermediate is also the precursor to VE that forms in the absence of a nucleophile during alkali pulping processes [2]. Generally, a nucleophile,

such as HS^- or anthraquinone, is necessary to cleave the β-O-4 linkages in the pulping process. When TBD was added, guaiacol was produced more effectively than other N-bases. We speculate that TBD may function as a nucleophile for the reaction, in addition to its role as a base in forming quinone methide. TBD and MTBD have essentially the same basicity but show a significant difference in guaiacol yield. Figure 3.1 illustrates the structure of the bases. The position 7 of MTBD and the position 1 (or 3) of TMG are hindered by methyl groups (Fig. 1), so only one exposed nitrogen atom with a lone electron pair exists in the structures of MTBD, TMG and DBU. It could be that the two exposed nitrogen atoms (N^1 and N^7) in TBD enable it to work more effectively as a dibasic nucleophile, attacking both the α- and β-carbon of quinone methide in a manner similar to hydrosulphide anion (HS^-) and thereby assisting the cleavage reaction.

Water is difficult to eliminate from ILs and could have been present as an impurity. When 10 μl H_2O (> 20-fold excess by mole to GG or TBD) was added into the TBD/[BDMIm]Cl system under the same conditions as above (Table 3.2, entry 3), the GG conversion, guaiacol, and EE yield were reduced. It is possible that TBD reacted with water in a manner similar to the reaction between DBU and water [17] and therefore the basicity of the system was lower and the form of nitrogen atoms in TBD were changed. Further study is needed to reveal the mechanism.

3.4 CONCLUSION

It was demonstrated that a series of organic N-base/[BDMIm]Cl systems are effective for promoting the decomposition of GG as a dimeric phenolic lignin model

compound. An enol-ether (EE), 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-2-propenol was found to be a primary decomposition product in all the systems. Interestingly, cleavage of the β-O-4 bond of GG increased significantly in the TBD/[BDMIm]Cl system. More than 90% of GG reacted in the TBD/[BDMIm]Cl system, including more than 40% β-O-4 bond cleavage product. TBD likely functions as both a base and nucleophile due to its unique exposed nitrogen atoms. As soon as the mechanism behind the activity of TBD is further elucidated, new processes of β-O-4 bond cleavage could be developed based on the suggested difunctional nucleophile model.

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Chapter 4: Cleaving the β-O-4 bonds of lignin model compounds in an acidic ionic liquid, 1-H-3-methylimidazolium chloride*

4.1 INTRODUCTION

The use of renewable feedstocks by the chemical industry has the potential to replace petroleum-based resources, possibly extending petroleum reserves and reducing the carbon footprint of a process or product [1]. Second and third generation biofuel production that is based on cellulosic feedstocks will require treating biomass to depolymerize the lignin and release the cellulosic fraction. It is generally accepted that lignin degradation is a rate-limiting step in lignocellulose degradation [2]. Lignin acts as the essential glue that gives plants their structural integrity and is a main constituent of lignocellulosic biomass (15-30% by weight, 40% by energy), together with cellulose and hemicelluloses [3]. However, lignin has received less attention relative to cellulose and hemicelluloses in the biorefinery of biomass. Lignin is rich in aromatic structures, therefore, some aromatic chemical compounds, such as vanillin, may be obtained from lignin [4], [5]. Moreover, the transformation of lignin has potential to produce fuels [6].

Lignin is a natural amorphous polymer with a complex structure (as shown in Figure 4.1), which is degraded inefficiently at present and generally burned (energetic utilization) in the course of recovery of chemicals in kraft pulping [7], [8]. Lignin is composed of phenylpropane monomers that link together primarily through the C-O linkage of α- and β-ether bonds [9]. The β-O-4 linkage is dominant among these bonds,

* Significant portions of this chapter have been previously published as: S. Jia, B. J. Cox, X. Guo, Z. C. Zhang, and J. G. Ekerdt, "Cleaving the β--O--4 bonds of lignin model compounds in an acidic ionic liquid, 1-H-3-methylimidazolium chloride: an optional strategy for the degradation of lignin.," *ChemSusChem*, vol. 3, no. 9, pp. 1078–84, Sep. 2010.

representing ~50% of the linkages in softwood lignin [8], [10]; therefore, efficiently cleaving the β-O-4 linkage could be an effective strategy for the degradation of lignin while preserving the aromatic character of the fragments.

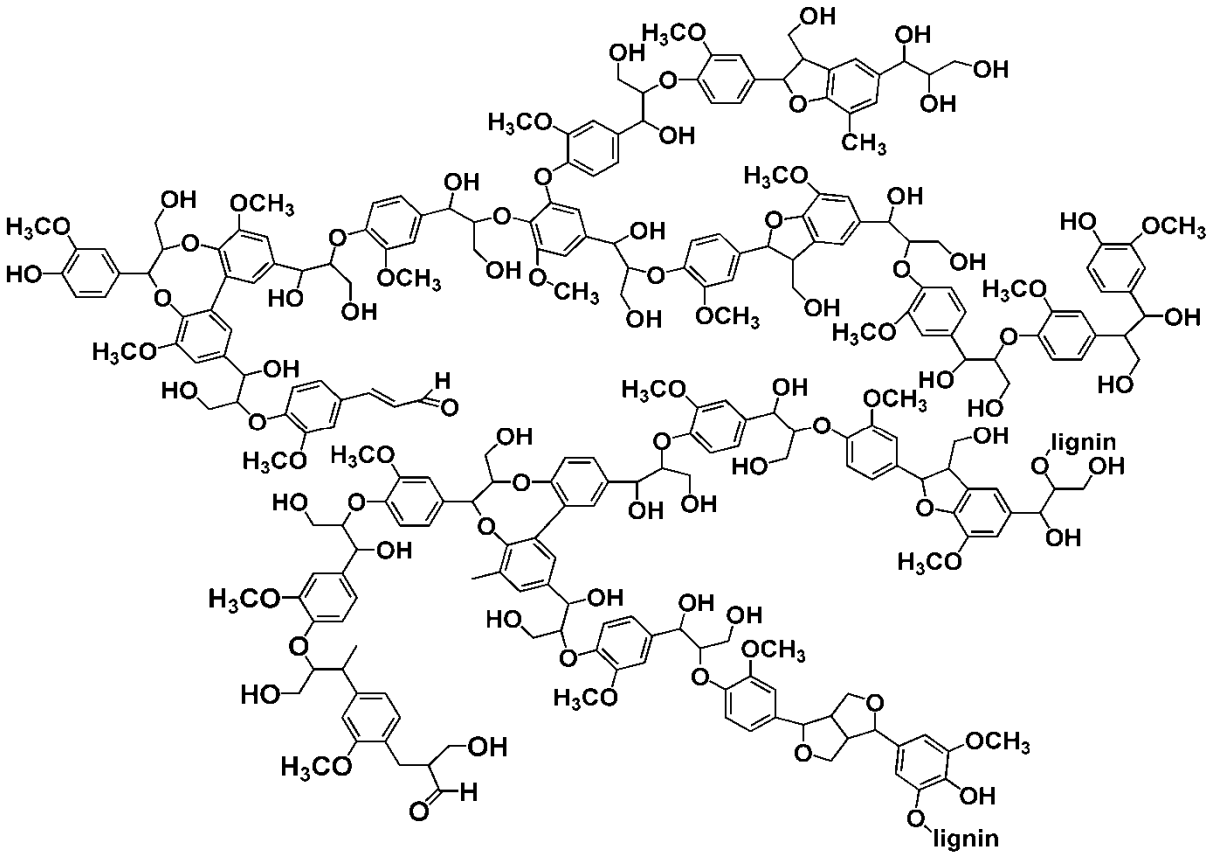

Figure 4.1: General structure of lignin

Acid and base catalyzed routes to lignin depolymerization are known; these fundamental processes involve strong acids, caustic alkali, sulfocompounds and volatile toxic solvents that can have negative effects on the environment. Kraft pulping, a common process for the depolymerization of lignin, mainly employs NaOH and NaSH (or anthraquinone) to cleave the β-ether bonds in lignin [9], [11]. Acid-catalyzed

hydrolysis is another method for cleaving the β-ether bonds of lignin [12]. Studies on the hydrolysis of β-ether bonds in phenylpropane dimer model compounds have been carried out with hydrochloric acid or $AlCl_3$ as the catalyst in dioxane-water or ethanol-water solvents [13], [14].

Ionic liquids (ILs) have attracted much attention as a medium for biomass conversion, primarily in the conversion of carbohydrates [15], [16]. However, few studies report on the reactivity of lignin in ILs. Recently, ILs have been found to be a direct wood pulp solvent capable of solubilizing lignocelluloses [17–20]. Guaiacylglycerol-β-guaiacyl ether (GG) is commonly employed as a model compound for the phenolic β-O-4 ether linkages in lignin. Recently, Kubo et al. found that an enol-ether (EE), 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-2-propenol, was the primary decomposition product from GG in dialkylimidazolium chloride and acetate ILs [21]. However, EE essentially is a dehydration product from GG, which implies these ILs did not cleave the β-O-4 bond. Binder et al. reported the dealkylation of alkyl substituted 2-methoxyphenols, which served as lignin model compounds, in a variety of ILs and realized up to 11.6% yield of the dealkylation product [22]. However, the high concentration of C-O bonds in lignin suggests cleaving these bonds, especially the β-O-4 bonds, is a more viable degradation strategy. Due to the complex chemical structure of lignin, one has to recognize the limitations of extrapolating results with simple model compounds featuring the β-O-4 bond to lignin. Nonetheless, model compounds, such as employed herein, facilitate understanding lignin chemistry.

Moreau et al. reported 1-H-3-methylimidazolium chloride ([HMIM]Cl) acted as both solvent and catalyst for the dehydration of sugars [23]. Since [HMIM]Cl is an easily synthesized and low-cost acidic IL from the BASIL technology [24], and a non-volatile IL, we explored its potential as the acid catalyst for the hydrolytic cleavage of β-O-4 linkages common in lignin. Herein we report initial results on the cleavage of β-O-4 bonds in both phenolic and non-phenolic lignin model compounds in [HMIM]Cl.

4.2 Results and Discussion

4.2.1 Cleavage of β-O-4 bonds in lignin model compounds

GG, a common dimeric lignin model compound, is employed for phenolic lignin units featuring the β-O-4 bond. Since guaiacol is liberated after the β-O-4 bond of GG is hydrolyzed (as shown in Figure 4.2), the extent of β-O-4 bond cleavage could be monitored by guaiacol yield. Water is ubiquitous in hydroscopic systems and it is needed for the hydrolysis reaction, so a controlled amount of water was added at a level that led to ~2 wt % H_2O. The C-2 protons of 1,3-disubstituted imidazolium cations are acidic [25], [26], therefore, two ILs, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-butyl-2,3-dimethylimidazolium chloride ([BdMIM]Cl, a C-2 substituted IL) were employed to test the effect of the C-2 proton. After 8 mg GG and 2.25 μl H_2O were heated at 130 ºC for 120 min in 100 mg of [BMIM]Cl or [BdMIM]Cl, less than 5% GG conversion was observed. No guaiacol was detected by HPLC; a trace amount of EE was detected by HPLC and verified by NMR. Although a controlled amount of H_2O was added into our system, the results are consistent with the low EE yield that was reported

in [BMIM]Cl after 180 min at 120 ºC [21], which indicates the C-2 proton has no effect on the GG conversion and hydrolysis of the β-O-4 bond.

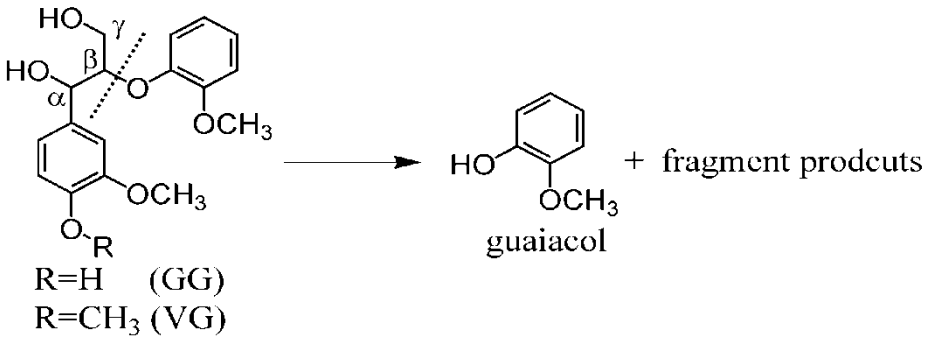

Figure 4.2: The cleavage of β-O-4 bond of lignin model compounds.

Figure 4.3a presents the results of reacting GG in [HMIM]Cl at various temperatures, in which 8 mg GG and 2.25 μl H_2O were added into 100 mg [HMIM]Cl for each experimental run. GG was effectively cleaved at temperatures as low at 110 °C, producing guaiacol in [HMIM]Cl. The guaiacol yield increased with reaction temperature, reaching 71.5% at 150 °C after 60 min. At the higher temperatures the guaiacol yield curves display a maximum, possibly because guaiacol underwent subsequent reactions [27]. The GG conversion is essentially 100% in all the experimental runs (shown in Figure 4.3a) except after 15 min at 110 °C, for which the GG conversion was 68.4%, and 6% yield of EE was detected. EE was not detected at longer times or higher temperatures.

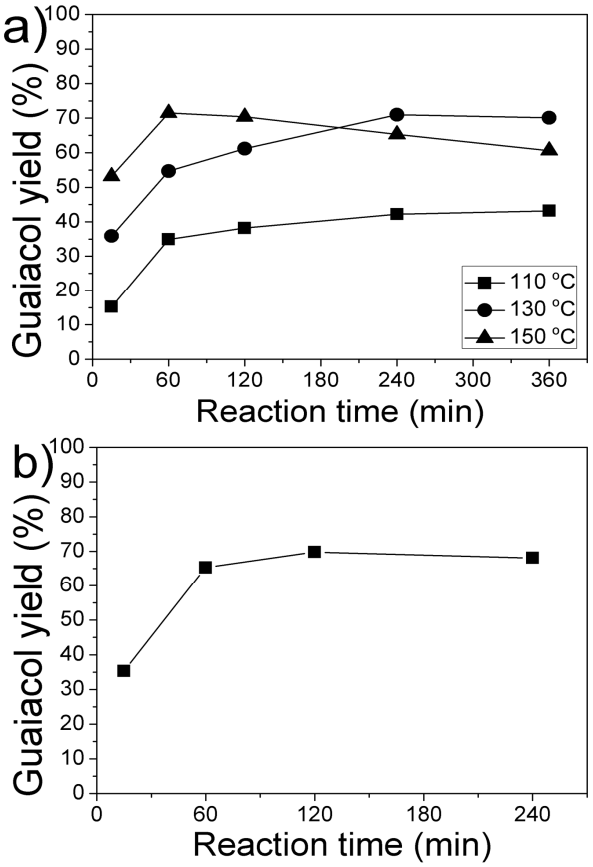

Figure 4.3: a) The effect of reaction temperature on cleavage of the β-O-4 bond of GG; and, b) cleavage of the β-O-4 bond of VG at 150 ºC.

In general, lignin consists of more etherified phenylpropane units, so we used veratrylglycerol-β-guaiacyl ether (VG) as a non-phenolic lignin model compound. The phenolic lignin model compound, GG, is considered to be more reactive. As illustrated in Figure 4.3b, the β-O-4 bond of VG was cleaved as steadily as GG at 150 ºC. The guaiacol yield was similar to that from GG and decreased a little after 120 min. The VG conversion also exhibited the same pattern as GG with essentially 100% conversion in all

the experimental runs. Both GG and VG were converted rapidly into intermediate products, some of which reacted to guaiacol (see below).

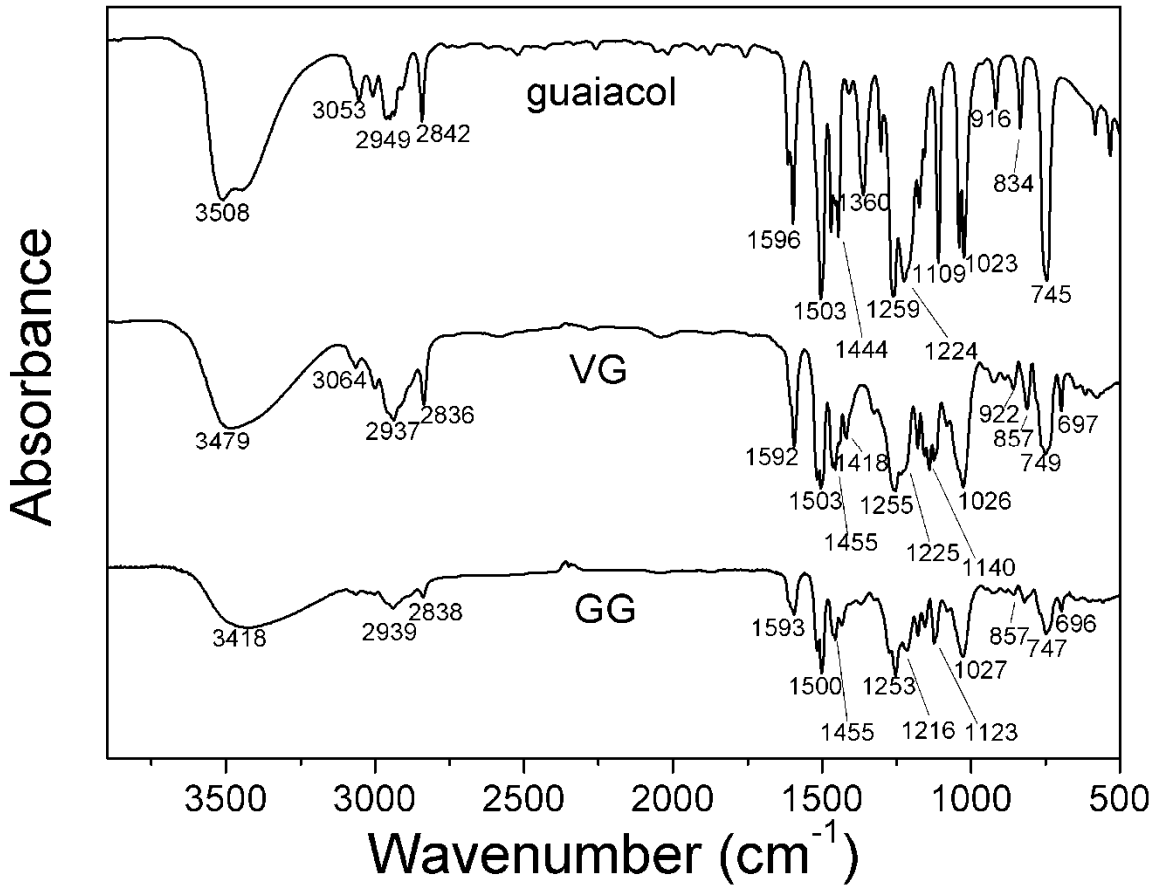

Figure 4.4: The FT-IR spectra of GG, VG and guaiacol.

Acid-catalyzed hydrolysis of GG and VG should also produce Hibbert's ketones [12], [28]. Figure 4.4 shows the FT-IR spectra of GG, VG and guaiacol. The absorbance around 3400-3500 cm^{-1} is associated with the hydroxyl group vibrational stretching modes for the three compounds; symmetric and asymmetric C-H modes produce the absorbances between ~2800-3000 cm^{-1}; absorbance bands around 1593 cm^{-1} and 1500

cm^{-1} are characteristic of aromatic rings; and absorbances at 1253 (1255 for VG) cm^{-1} and 1027 (1026 for VG) cm^{-1} are the C-O vibrational stretching vibrational bands. After the reaction of GG and VG in [HMIM]Cl at 150 °C for 60 min, the product mixtures were extracted by ethyl ether, and ethyl ether was removed before the FT-IR test. As illustrated in Figure 4.5, the FT-IR spectra of the product mixtures from GG and VG retain many of the same absorbance features as Figure 4.4 except for the absorbance around 1731 cm^{-1}, which is the characteristic stretching mode for the C=O bond and implies a ketone or aldehyde were produced. These results are consistent with previous work [12], [28], in which Hibbert's ketones were formed by the acid-catalyzed hydrolysis of GG and VG. The absorbance at 1682 cm^{-1} may result from the conjugate effect between the C=O bond and the benzene ring after the isomerisation of Hibbert's ketones [12], [29].

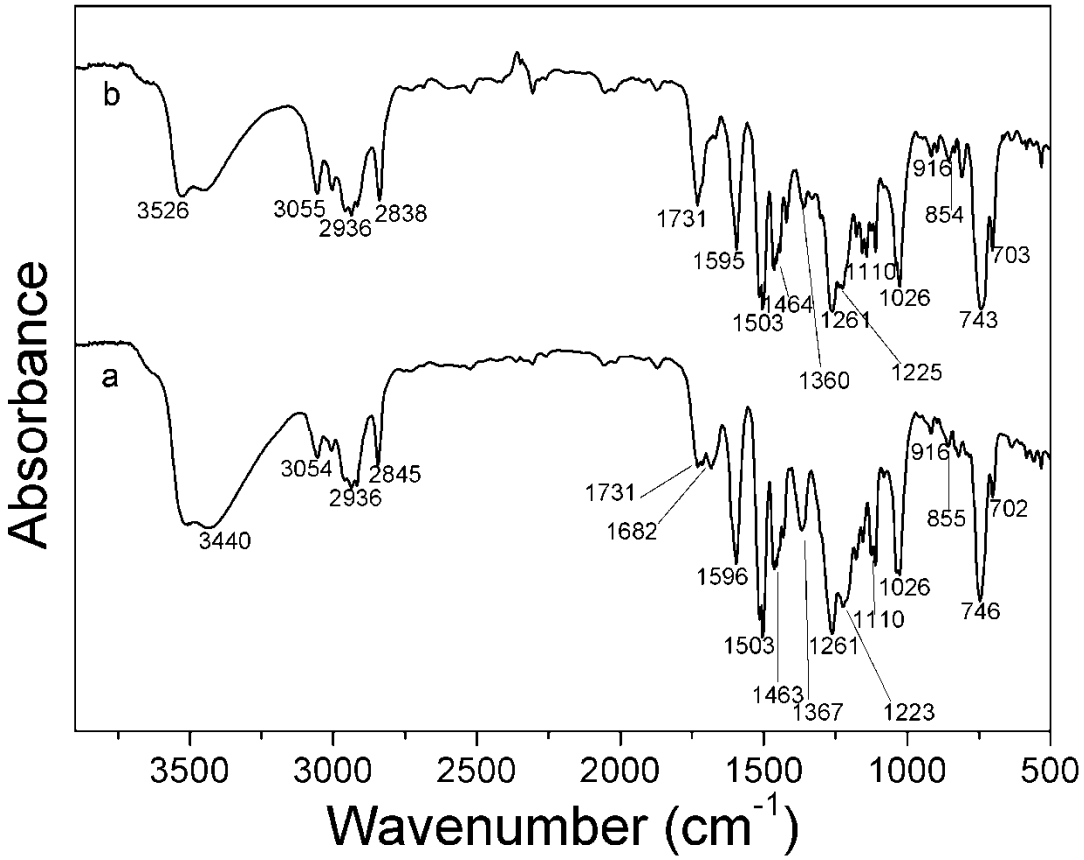

Figure 4.5: The FT-IR spectra of (a) product mixture from GG, (b) product mixture from VG.

The product mixtures were also monitored by LC-MS. When GG was tested, we found two LC peaks that had a strong $(m+H)^+/z$ of 197 in the MS. This LC-MS species is associated with Hibbert's ketones [12], [28], [29], which are companion products from GG after elimination of guaiacol. When VG was tested, two LC peaks with $(m+H)^+/z$ of 211 were detected in the MS, which are possibly etherified Hibbert's ketones from VG. The Hibbert's ketones were not established quantitatively.

The use of dilute solutions for the conversion of biomass may limit the efficacy of the process. A more desired approach would allow the processing of highly concentrated

liquids to minimize the solvent volume and concentration steps associated with solvent removal [30]. In this work, the effect of substrate concentration was also tested by increasing the amount of GG (or VG) from 8 wt% to 32 wt%. As illustrated in Figure 4.6a, after the system of GG (or VG) and water (molar ratio 5:1 to GG or VG) in 100 mg [HMIM]Cl was heated at 150 ºC for 60 min, the guaiacol yield was reasonably constant at ~70% and ~65% for GG and VG, respectively.

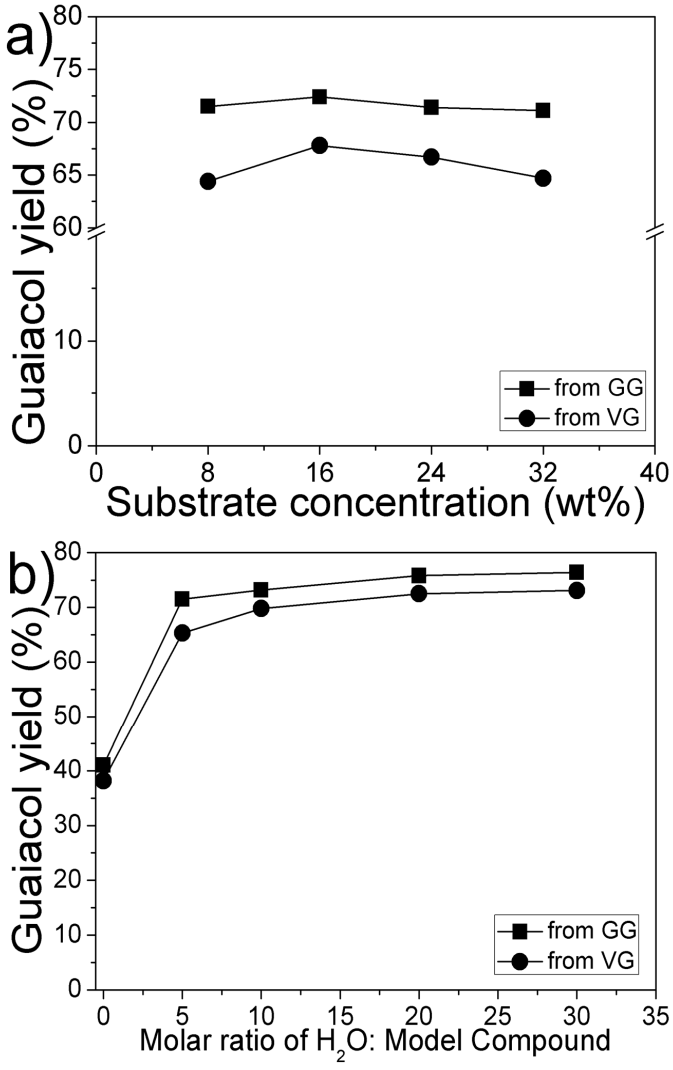

Figure 4.6: a) The effect of substrate concentration on cleavage of the β-O-4 bonds of GG and VG; and, b) the effect of water concentration on cleavage of the β-O-4 bonds of GG and VG.

Both GG and VG were used in tests to measure the effect of water concentration on the yield. These experiments were run at 150°C for 60 min with 8 mg GG (or 8.4 mg VG) and 100 mg [HMIM]Cl, with different amounts of water. As illustrated in Figure 4.6b, at a molar ratio of 5:1, the yield of guaiacol was 71.5 and 65.3% from GG and VG,

respectively. When the water was increased to a 30:1 ratio, the guaiacol yield from GG and VG was 76.4 and 73.1%, respectively, while the yield dropped to 41.0 and 38.2% from GG and VG, respectively, when no water was added. A small but significant increase in β-O-4 bond cleavage results from an increase in available water. As the water is removed, the guaiacol yield drops because the hydrolysis will not occur without water present. The reaction is not completely stopped by removal of water, because the possible dehydration of lignin model compounds produces water, which then can hydrolyze the β-O-4 bonds [12], [21].

Figure 4.7 presents the results of recycling [HMIM]Cl for β-O-4 bond cleavage of GG and VG. After reacting 8 mg GG (or 8.4 mg VG) and 2.25 μl H_2O in 100 mg [HMIM]Cl at 150 ºC for 60 min, the products were extracted at 100 ºC by successively adding methylisobutylketone (MIBK) 10 times, using 0.6 ml of MIBK each time. After the extraction, the appropriate amounts of GG (or VG) and H_2O were added into the [HMIM]Cl directly and without extra treatment. The guaiacol yields changed less than 3% in subsequent runs, which may indicate it is feasible to recycle the IL without loss of activity.

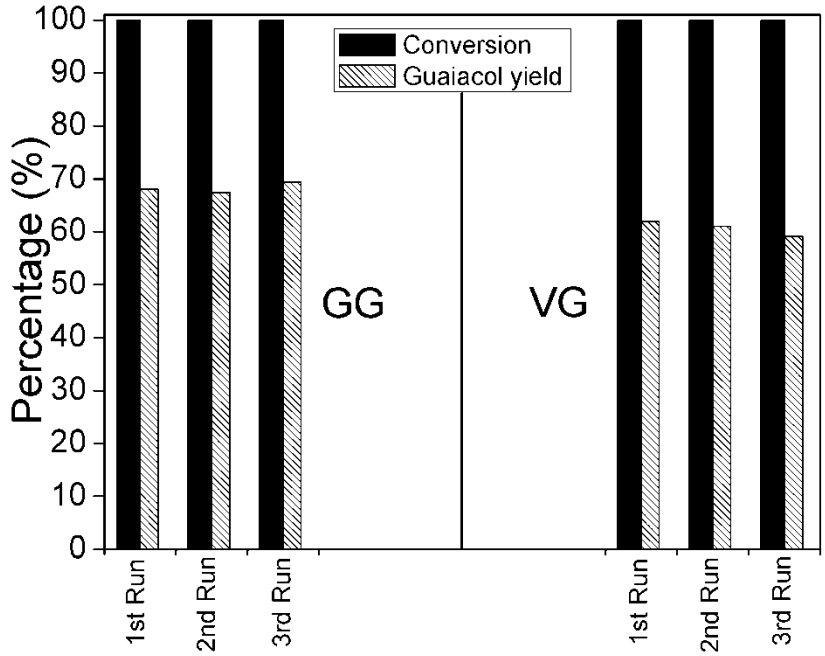

Figure 4.7: Recycling tests on cleavage of the β-O-4 bonds of GG and VG in [HMIM]Cl.

It is important to note the separation conditions employed for the recycle tests were not optimized and some loss of [HMIM]Cl and cross contamination occurred. In six parallel control experiments [HMIM]Cl was contacted with MIBK using the procedure listed above. The average residue of MIBK was 7.3 mg in per 100 mg [HMIM]Cl after the extraction. After removing the solvent by vacuum, the loss of [HMIM]Cl was 1.3 mg per 100 mg. The MIBK was tested by adding an indicator (methyl orange) and did not show to be acidic.

The hydrolysis of the β-O-4 bonds of GG and VG was also carried out in a high boiling solvent, dimethylsulfoxide (DMSO), in combination with HCl. The amount of HCl was chosen at a catalytic amount and was somewhat arbitrary. The hydrolysis of

GG and VG was expected [13], [14]. As can be seen in Table 1, after heating GG (or VG) and H_2O in DMSO with HCl (10 mol% to GG or VG) as the catalyst at 150 ºC for 60 min, 55.2% guaiacol yield was observed from GG with 100% GG conversion while 17.7% guaiacol yield was observed from VG with 61.3% VG conversion. The guaiacol yield from VG increased to 39.1% with 93.8% VG conversion when reaction time was increased to 120 min. Higher HCl concentration (Table 1, Entries 2, 4 and 6) appears to have a minor effect on the hydrolysis of GG and VG. The lower guaiacol yield at 100% conversion as compared to that in [HMIM]Cl implies more undesired reactions happened in DMSO under the conditions explored herein. Further, a more complex process is necessary for the separation and purification of products from DMSO, which could increase the production costs. In contrast, an IL approach will likely have advantages in this case, such as distillation or successive extraction by organic solvents from the ionic liquid phase.

Table 1. The results on cleavage of the β-O-4 bonds of GG and VG in DMSO with HCl as the catalyst

Entry	Lignin model compound	Time (min)	Conversion (%)	Guaiacol yield (%)
1[a]	GG	60	100.0	55.2
2[b]	GG	60	100.0	57.0
3[a]	VG	60	61.3	17.7
4[b]	VG	60	66.2	19.4
5[a]	VG	120	93.8	39.1
6[b]	VG	120	100.0	40.3

[a] 0.025 mmol lignin model compound and 0.125 mmol H_2O were added into 100 mg DMSO with HCl (10 mol% to lignin model compound) and heated at 150 ºC. [b] 0.025 mmol lignin model compound and 0.125 mmol H_2O were added into 100 mg DMSO with HCl (20 mol% to lignin model compound) and heated at 150 ºC.

Table 4.1: The results on cleavage of the β-O-4 bonds of GG and VG in DMSO with HCl as the catalyst.

Acid catalysis is a common treatment that is widely used in biomass transformation, such as the hydrolysis and depolymerization of cellulose [31–35], and the conversion of sugars [15], [36–39]. The work reported herein employs an acidic IL to treat model compounds that have the β-O-4 bond common in lignin. Additional studies are required to establish the potential for acidic IL as catalysts for lignin depolymerization.

4.2.2 Possible Reaction Pathways for β-O-4 Bond Cleavage

The studies reported above revealed essentially 100% conversion of GG and VG at all but the lowest temperature and shortest time. Guaiacol yield is below 100% at all conditions due to consecutive condensation reactions as discussed below. EE was only

detected at 6% yield with GG at 15 min and 110 °C. Acidic conditions can lead to the formation of EE from GG [12], [28], [29], and EE could undergo a subsequent hydrolysis reaction, leading to the cleavage of β-O-4 bond of GG to produce guaiacol and a Hibbert's ketone [12], [28], [29]. EE is also reported to be unstable under acidic conditions [21], which may explain why EE was not detected in most of the experiments reported herein.

To account for the other products that led to a reduced guaiacol yield, studies were conducted at 110 °C with GG in [HMIM]Cl to determine additional products that could have formed between 0 and 60 min. First, one would expect a condensation reaction involving the hydroxyl groups in GG. In fact, LC-MS showed a peak with $(m+H)^+/z$ of 623, which is consistent with GG dimers coupled by ether linkages formed from the condensation reaction. Additional products with $(m+H)^+/z$ values of 498 and 303 and some heavier products were also detected by LC-MS. The UV absorbance cross sections for the GG dimers, and those for the $(m+H)^+/z$ 303 and 498 peaks were assumed equal to GG. As illustrated in Figure 4.8, EE was the main product detected at the onset of the reaction and showed a maximum after 5 min. The GG dimer products display a maximum at 25 min. The subsequent decrease of the dimers most likely resulted from the cleavage of the β-O-4 bond in the dimers to release guaiacol. The unidentified product with a $(m+H)^+/z$ 498 could be the product formed after one guaiacol is liberated from a GG dimer. In addition, the unknown product with a $(m+H)^+/z$ 303 and a small amount of other coupling products were all formed in the reaction. However, further study is needed

to solve their structural details. Since VG is less reactive than GG, VG was reacted at 130 ºC, and we found similar products as GG.

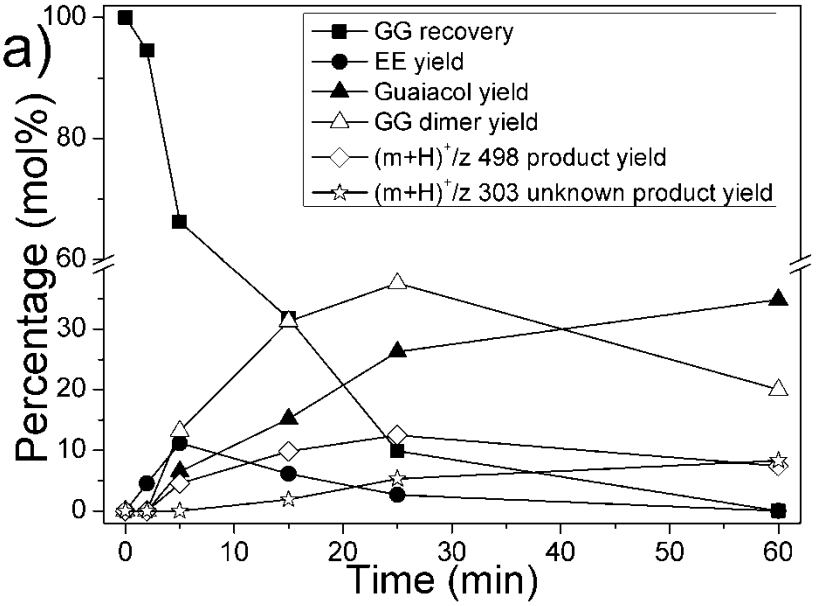

Figure 4.8: GG recovery and product yields for GG reaction at 110 ºC (The response factors of GG dimers, $(m+H)^+$/z 498 and 303 products are assumed to equal to that of GG).

Figure 4.9 compares the various products after 60 min for the temperatures used herein. At 60 min, the GG conversion is 100 %. More of the GG dimers were consumed with increasing temperature. The $(m+H)^+$/z 498 product yields also decreased with increasing temperature and this could be the result of subsequent reactions of this compound. The unidentified product ($(m+H)^+$/z 303) concentration remained relatively constant, which indicates this product is stable under the reaction conditions and may not lead to the β-O-4 bond cleavage.

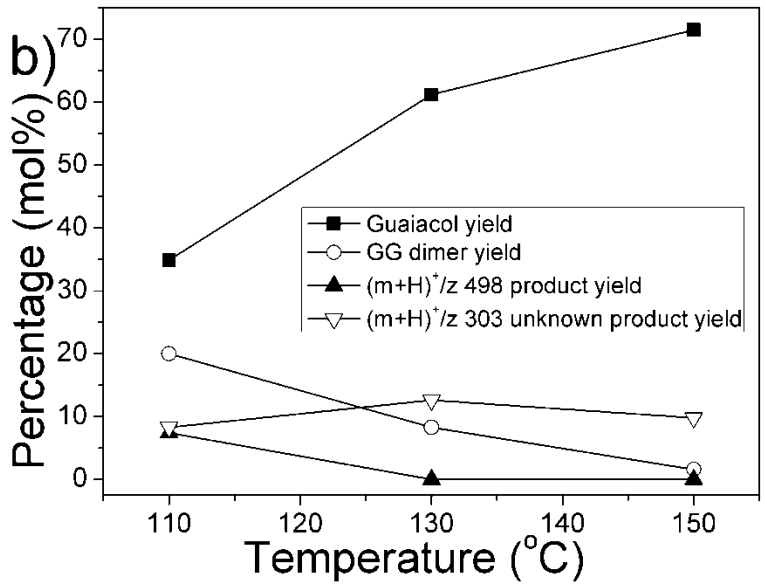

Figure 4.9: Product yields for GG reaction at different temperatures after 60 min (The response factors of GG dimers, $(m+H)^+$/z 498 and 303 products are assumed to equal to that of GG).

Based on the results above, we speculate EE (or the EE analog from VG (VEE)) and GG dimers (or VG dimers) are possible intermediates in the reaction of GG (or VG), leading to the β-O-4 bond cleavage. The $[HMIM]^+$ cation was reported to be Brønsted acidic [39], which implies H^+ could exist in the system. Based on this, we propose one possible acid-catalyzed mechanism for the hydrolysis of β-O-4 bonds of GG and VG via the possible EE (VEE) and dimer intermediates, as shown in Figure 4.10. In the proposed pathways, acid-catalyzed dehydration and coupling occur first, which explains why the β-O-4 bonds can be hydrolyzed in [HMIM]Cl without added water. Water could attack the β-carbon of the proposed intermediates, leading to the β-O-4 bond cleavage. EE hydrolysis in acids is reported [12], [28]. GG and VG dimers could undergo hydrolysis to produce guaiacol and Hibbert's ketones. More added water could increase

the rate for the hydrolysis step, which accounts for the slightly higher guaiacol yield (Figure 4.6b).

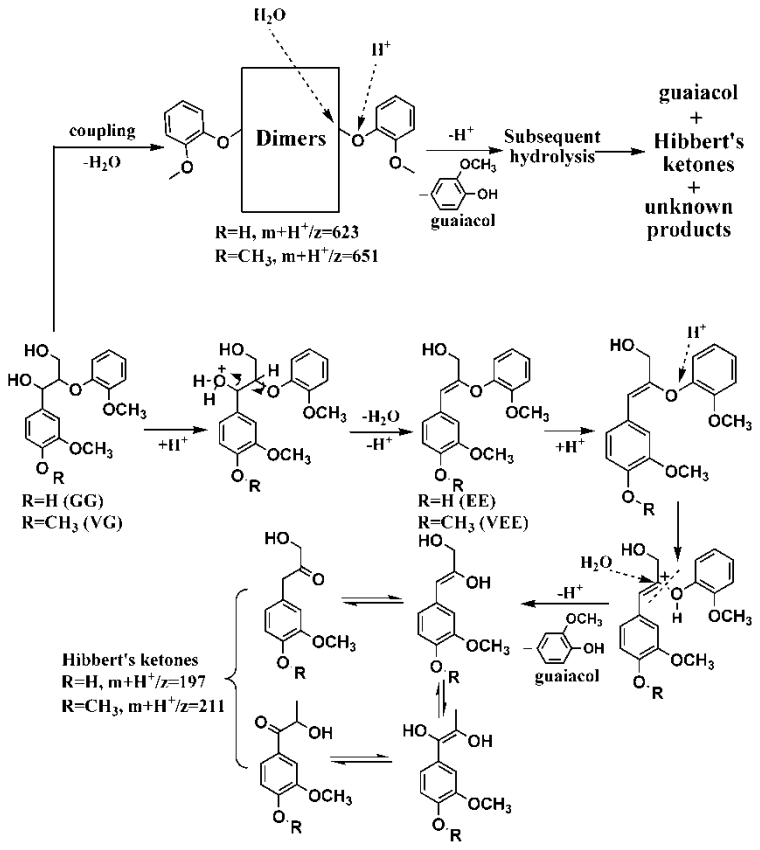

Figure 4.10: Proposed acid-catalyzed mechanism for hydrolysis of the β-O-4 bonds of GG and VG.

4.3 CONCLUSION

In conclusion, we demonstrate an efficient method for the cleavage of β-O-4 bonds of phenolic and non-phenolic lignin model compounds in an acidic ionic liquid, [HMIM]Cl. More than 70% of the β-O-4 bonds of both GG and VG reacted with water to produce guaiacol at 150 °C. There was little change in the reactivity of GG and VG as

the substrate concentration increased from 8 wt% to 32 wt%. The ionic liquid solvent/catalyst could be reused without extra treatment or appreciable loss of activity. The presence of water is necessary for efficient β-O-4 bond cleavage, although after a critical amount, additional water does not increase reactivity. EE (or VEE) and GG (or VG) dimers were also formed, some were further reacted to form guaiacol and Hibbert's ketones. Heavier unidentified products are likely humins. Guaiacol was formed either directly from GG (or VG) monomers, or from the corresponding condensed dimer or oligomers of GG (or VG). The method described herein may have potential to degrade real lignin (or lignocelluloses).

4.4 EXPERIMENTAL SECTION

Materials: Guaiacylglycerol-β-guaiacyl ether (GG 99%) and 3,4,5-trimethoxybenzaldehyde (TMBA 98%) were purchased from Tokyo Chemical Industry Co. Ltd. Veratrylglycerol-β-guaiacyl ether (VG 97%) was purchased from Astatech Inc. 1-H-3-methylimidazolium chloride ([HMIM]Cl 95%), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl 95%) and 1-butyl-2,3-dimethylimidazolium chloride ([BdMIM]Cl 97%) were purchased from Sigma-Aldrich. Methylisobutylketone (MIBK 99.5%) was purchased from Acros Organics. Dimethylsulfoxide (DMSO 99%), ethyl ether (99.9%) and hydrochloric acid (HCl 36.9 wt%) were purchased from Fisher Scientific.

Typical procedure: [HMIM]Cl was vacuum dried before use. 100 mg [HMIM]Cl was added into each vial (0.3 ml) with a magnetic stirrer. Then 8 mg (0.025 mmol) GG and 2.25 μl H_2O (0.125 mmol) were added into each vial. The vials were sealed, inserted

into a Reacti-Therm heating and stirring module (Thermo Scientific) and stirred at 400 rpm for a set time at the reaction temperature. Then the vials were cooled down in ice water, diluted with H_2O-acetonitrile (1:9 by volume) and analyzed by high pressure liquid chromatography (HPLC).

Analysis method: HPLC was performed on a Dionex Ultimate 3000 series (UV 280 nm) with a Phenomenex Gemini C6-phenyl column (50×4.6 mm, 3 μm). H_2O-acetonitrile was used as the mobile phase. TMBA was added as the internal standard for the quantitative calculations. Liquid chromatography-mass spectroscopy (LC-MS) was performed on an Agilent 6130 single quadrupole mass spectrometer interfaced to an Agilent 1200 Series HPLC with a diode array detector and a Gemini C18 column (50 x 2.1 mm). NMR was performed on a Varian INOVA 500 MHz series system. FT-IR spectra were obtained on a Nicolet Avatar 330 FTIR spectrometer with a Smart Performer ATR attachment.

$$\text{Conversion (mol\%)} = (1 - \frac{\text{remaining GG or VG detected by HPLC}}{\text{added GG or VG}}) \times 100\%$$

$$\text{Guaiacol yield (mol\%)} = \frac{\text{produced guaiacol detected by HPLC}}{\text{added GG or VG}} \times 100\%$$

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Chapter 5: Catalytic degradation of lignin model compounds in acidic ionic liquids: Hammett acidity and anion effect*

5.1 INTRODUCTION

Lignocellulosic biomass is composed primarily of cellulose, hemicellulose, and lignin. The lignin is a complex, amorphous polymer that acts as glue that holds together the cellulose of plant matter [1]. The complexity of lignin derives from the many ways that the phenylpropane monomers can polymerize. Because there are multiple places on the monomer that are available for polymerization, the structure of lignin contains a number of different kinds of linkages [2]. The most common of these is the β-O-4 ether linkage (representing 48 to 60% of linkages in lignin) [3]. The polymer is also rich in aromatics and contains a disproportionate fraction of the energy in biomass compared with cellulose (15-30% by weight, but roughly 40% by energy) [4].

Lignin is also a major inhibitor of decomposition of plant material in nature. Because of this recalcitrance, lignin is a primary hurdle in the successful conversion of biomass into value-added products such as fuels or commodity chemicals [5]. Future generations of biomass based products will require the effective depolymerization of lignin to facilitate easier access to the cellulose [2]. Currently, the pulp and paper industry primarily uses a process called kraft pulping that relies on a strong base, sodium hydroxide, and a nucleophile, generally sulfur compounds, at high temperatures and pressures to degrade lignin and separate it from cellulose. The resulting lignin is then

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burned on site as a low grade fuel [1], [4]. Other methods of lignin degeneration rely on organic solvents, often coupled with acidic conditions to degrade and remove lignin from raw biomass [6], [7].

There has been a recent increase in the study of ionic liquids (ILs) as solvents and catalyst in a variety of fields. An IL is a substance that is composed entirely of anions and cations, which exists as a liquid at or below 100 °C. There are many different ILs, based a number of cations [8], [9]. These compounds have garnered recent attention due to their novel properties. For instance, ILs have essentially no vapor pressure and, with only some exceptions, possess high chemical stability [10]. Based on the specific combination of anions and cations, the properties of an IL can be "tuned" to a specific task. For example, miscibility with various solvents, melting point, acidity, and solubility of a catalyst can be adjusted [8], [11], [12]. ILs have also been shown to be attractive media for catalysis and task specific ILs can even be used as both solvent and catalyst [12], [13]. Interestingly, a number of ILs have been shown to completely dissolve biomass [4], [14], [15].

The ability of ILs to dissolve biomass has potential to contribute to the successful utilization of bioresources. By homogenizing biomass, the chemistry necessary to convert plant matter into value-added products can be performed on the entire structure of the biomass instead of just the surface. This idea has led to significant research in depolymerization of cellulose and degradation of sugars in ionic liquids [16–18]. However, limited efforts have been directed towards the degradation of lignin in ILs.

More of the lignin-related effort has been directed at the reaction of model compounds featuring the β-O-4 ether and C-C linkages common to lignin [19–26].

Recently, a study by Jia, et al., demonstrated that an acidic IL, 1-methylimidazolium chloride (HMIMCl), could be used to cleave the β-O-4 ether linkage in the lignin model compounds guaiacylglycerol-β-guaiacyal ether (GG) and veratrylglycerol-β-guaiacyl ether (VG) [26]. The degradation of the model compound proceeded through both monomeric and dimeric intermediates before guaiacol was released through the hydrolysis of the β-O-4 ether bond. The work presented herein investigates how the acidity and composition of 1-methylimidazolium-based acidic ILs affect degradation of lignin through the use of model compound studies.

5.2 MATERIALS AND METHODS

5.2.1 Material synthesis and purchase

1-methylimidazolium bromide (HMIMBr), 1-methylimidazolium hydrogen sulfate ($HMIMHSO_4$), and 1-methylimidazolium tetrafluoroborate ($HMIMBF_4$) were made using the same method. In a typical synthesis, roughly 10 g (~0.12 mol) of 1-methylimidazole was mixed with 40 ml of water and chilled in an ice bath. Then a slightly sub-stoichiometric quantity of strong acid (hydrobromic, sulfuric, or tetrafluoroboric acid) at 50 weight% concentration was added dropwise with intermittent stirring. Because it was important to eliminate any residual acid, care was taken that the initial mixture contained a slight excess of 1-methylimidazole. All appropriate precautions should be observed when working with strong acids. After the addition, the

mixture was allowed to warm up to room temperature over the course of an hour. The water was then removed using an aspirator and mild heating. The resulting IL was then washed twice with 10 ml of toluene and dried on a Schlenk line with gentle heating. In the case of $HMIMBF_4$, the IL needed to be dissolved in acetonitrile and filtered to remove an unidentified white precipitate. The ILs were stored in a desiccator and the purity verified using H-NMR. Although exact melting point data were not obtained, all ILs mentioned here melted well below 100°C.

HMIMCl (95%) and 1-butyl-3-methylimidazolium hydrogen sulfate ($BMIMHSO_4$) (95%) were purchased from Sigma- Aldrich. Guaiacylglycerol-β-guiacyl ether (GG) (>99%) and 3,4,5-trimethoxybenzaldehyde (TMBA) (>98%) was purchased from TCI America. Veratrylglycerol-β-guaiacyl ether (VG) (97%) was purchased from Astatech. Hydrobromic acid (49%), tetrafluoroboric acid (50%), sulfuric acid (98%), toluene (99.5%), dimethylsulfoxide (DMSO) (99%), and acetonitrile (99%) were purchased from Fisher scientific. All chemicals were used without further purification.

5.2.2 Acidity measurements

To approximate the acidity of a pure IL, spectroscopic measurements were used to determine the Hammett acidity of acid indicator solutions [27]. Other researchers have used similar methods to compare IL acidity [13], [28]. Because the ILs were either solid or too viscous at room temperature, a series of dilutions was used and the acidity of the pure substance was extrapolated. In a typical series of experiments to approximate the Hammett acidity of an IL, the IL was diluted in dimethylsulfoxide (DMSO) in ratios of 0.5, 1.0, 2.0, 5.0, 7.0, and 10.0 mmol of IL per ml of DMSO. The density of each of

these solutions was measured. Additionally, a 25 volume% solution of sulfuric acid in DMSO was made as an acid standard. From each of these solutions, a 1.0 ml sample was mixed with 30 µl of 0.02 M solution of 3-nitroaniline (*pKa*=2.50) in DMSO while another 1.0 ml sample was mixed with 30 µl of pure DMSO as a standard. These mixtures were made under ambient conditions and then sealed with Parafilm®. While no water was added, it should be noted that these ILs are hygroscopic so small amounts of water were unavoidable. In the case of hydrolyzable ions, the presence of water can contribute to acidity in ILs [29]. The effect of small amounts of water on the acidity measurements reported herein should be minimal. Each sample was measured on a Cary 300 series UV-vis spectrometer. Based on these measurements, the ratio of protonated indicator to deprotonated indicator, $[HI^+]/[I]$, could be measured. The UV-vis data were processed to account for peak shifting by minimizing the difference in $[HI^+]/[I]$ values as calculated over the range of the data and the recorded $[HI^+]/[I]$ values were the average of these. The Hammett acidity of each solution was calculated with the formula:

$$H_0 = pKa_I - \log_{10}\left(\frac{HI^+}{I}\right),$$

where pKa_I is the pKa of the indicator. The density was measured by weighing three 100 µl samples of solution. The average of the three densities was then used to determine the volumetric concentration of each solution and a curve for density versus mole fraction was extrapolated to a mole fraction of 1.0 to estimate the density of the pure IL at room temperature.

5.2.3 Reaction of lignin model compounds in ILs

The procedure for the reaction of a lignin model compound in an acidic IL is as follows. All reactions were carried out in a Reacti-Therm heated/stirred module (Thermo Scientific) using 0.3 ml sealed glass vials. A sample of IL was melted in a hot water bath and transferred to a vial. This vial was heated to the reaction temperature (110 °C, 130 °C, or 150 °C) and 170 μl of IL transferred to a reaction vial along with a stir bar. The reaction vial was sealed and left to heat to reaction temperature for approximately 10 min. Then 6.0 mg (0.0188 mmol) GG was added along with 2.0 μl (0.111 mmol) water before the vial was returned to the reactor. Time was measured from when the vial was returned to the reactor. Once the allotted time had passed, the vial was removed and placed in an ice water bath. The sample was diluted with 2 ml of a 1:1 acetonitrile/water mixture with a small amount of 3,4,5-trimethoxybenzaldehyde as an internal standard. These were then analyzed on a Dionex Ultimate 3000 series HPLC using a Phenomenex Gemini C6-phenyl column (50x4.6 mm, 3 μm) and acetonitrile/H_2O as the mobile phase. Conversion was calculated by measuring the amount of model compound remaining and cleavage of the β-O-4 bond was tracked by the yield of guaiacol. All yields are calculated with respect to the theoretical maximum from the model compound.

5.3 RESULTS

5.3.1 Acidity measurements

Acidity did not vary much between the different ILs. As shown in Figure 5.1, the ILs exhibit acidities that reside within about a half decade on the Hammett acidity scale.

The most acidic IL is HMIMCl, with an H0 value of 1.48. The H0 values of other ILs, HMIMBF4, HMIMHSO4, HMIMBr, and BMIMHSO4, are 1.70, 1.99, 2.04, and 2.08 respectively. It is not unexpected for the HMIM based ILs to have similar acidity because the same Brønsted acidic cation is present in each IL. One source of error in determining the IL acidity may be the extrapolated molar density of the acidic cation in the pure IL. A denser IL will have a higher concentration of acid sites (lower H0), which does contribute to some of the differences. Ideally, the acidity should be established at the reaction temperatures but high temperature UV-vis measurement was beyond our experimental capabilities.

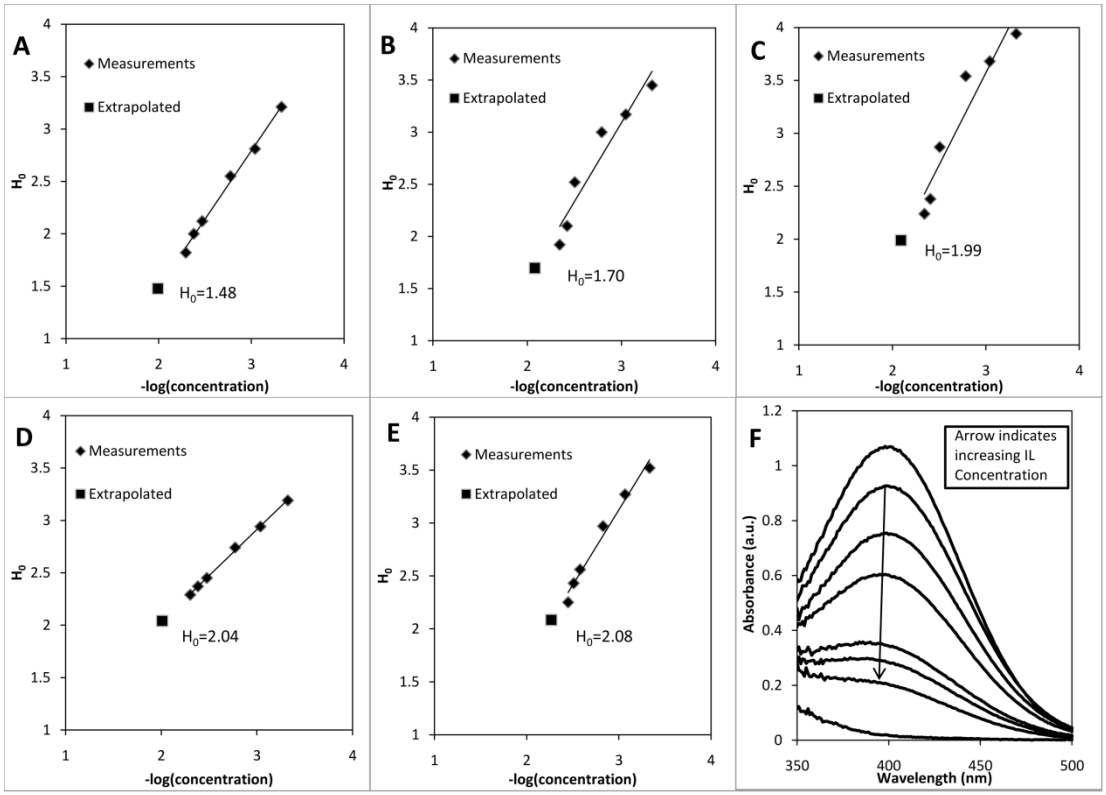


Figure 5.1: Acidity of (A) HMIMCl, (B) $HMIMBF_4$, (C) $HMIMHSO_4$, (D) HMIMBr, and (E) $BMIMHSO_4$. (F) Sample UV-vis results of the HMIMCl acidity measurements. The top and bottom curve are the DMSO and acid standards, respectively, and the curves between them have decreasing absorbance with increasing IL concentration.

5.3.2 Reaction of lignin model compounds

The phenolic lignin model compound, GG, was tested at 110 °C, 130 °C, and 150 °C. The non-phenolic model compound, VG, was only tested at 150 °C to compare its behavior to that of GG. From Figure 5.2, it is apparent that there is a large difference in hydrolytic reactivity in the different acidic ILs. In most cases, the conversion of GG was at or near 100%, so the important attribute in each reaction is the guaiacol yield. This level of conversion was also observed by Jia, et al., in a similar system with the major

intermediate being a dimer of GG or VG [26]. When the β-O-4 bond is hydrolyzed, guaiacol is produced, so the quantity of guaiacol produced in each reaction is a convenient way to track the cleavage of the β-O-4 ether linkage. Additionally, Figure 5.3 shows that the guaiacol yield increases over time, even after all of the original model compound has been consumed. It has been shown that there are a number of different pathways, with associated intermediates, that lead to the release of guaiacol from GG [6], [7], [26]. The mechanism for acid catalyzed hydrolysis of the β-O-4 ether bond (Scheme 5.1) begins with the transformation of the model compound into either an enol ether (EE) or vinyl ether (VE) isomers through the release of water and, in the case of VE, formaldehyde. The intermediate then undergoes ether bond hydrolysis to release guaiacol and a carbonyl compound that, in the case of the EE pathway, undergoes rearrangement to form Hibbert's ketones [30]. The GG molecules can also dimerize before undergoing dehydration and ether bond hydrolysis [26], [31]. While the $HMIMBF_4$ and $HMIMHSO_4$ always produced lower yields of guaiacol, the activities of HMIMCl, HMIMBr, and $BMIMHSO_4$ with respect to cleaving the β-O-4 ether bond varied significantly with temperature. HMIMCl at 150 °C produced the highest yield of guaiacol with a yield of 82.5%.

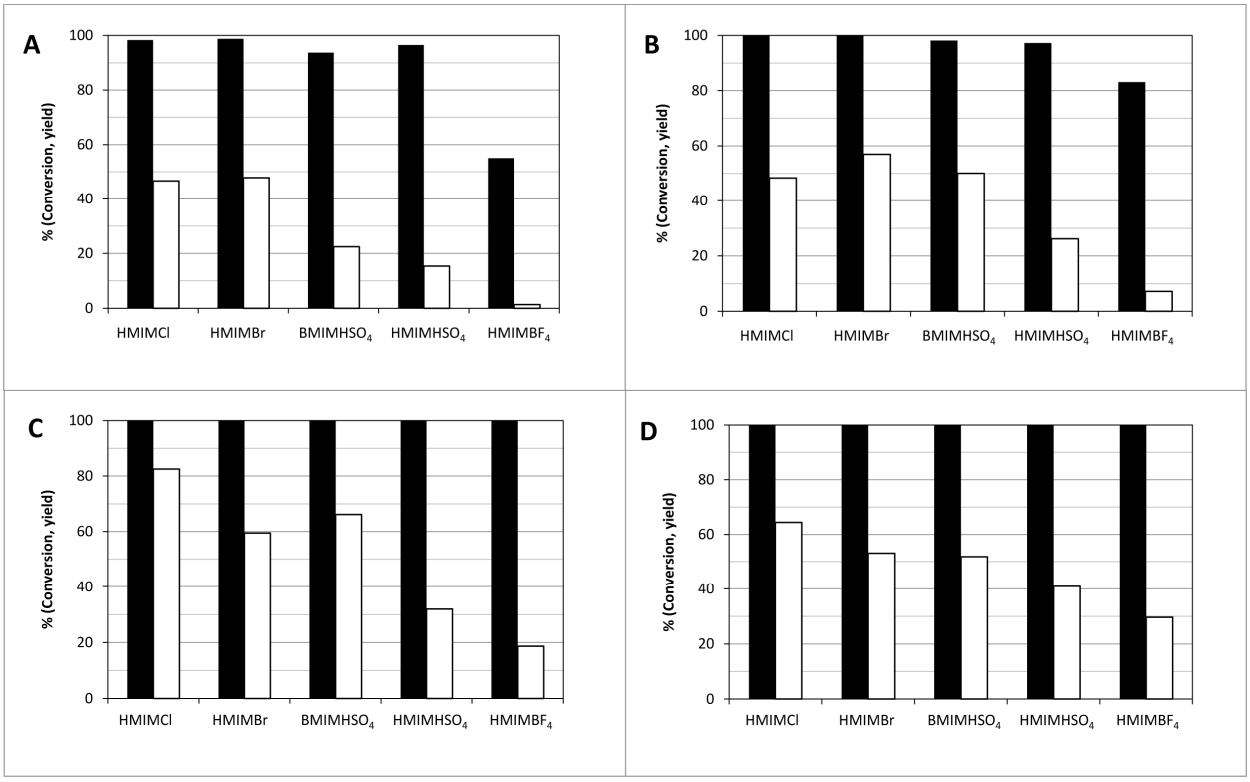


Figure 5.2: Conversion (■) and guaiacol yield (□) after 20 min under the conditions: (A) 110°C, GG as model compound. (B) 130°C, GG as model compound. (C) 150°C, GG as model compound. (D) 150°C, VG as model compound.

Using an LC/MS, several intermediate products were identified in the reaction mixtures. These results are displayed in Table 5.1. Most products became protonated when ionized in the MS, so the m+H/z values are given. The intermediate products confirm the acid catalyzed mechanism and are in agreement with previous research [26]. The dimers of GG and VG were observed as m/z signals instead of m+H/z and the VG dimer appeared as a m/z 668 peak in all reactions tested. A second dehydration product of the model compound, observed at m+H/z 285 for GG and 299 for VG, was present as both a product and as a fragment formed in the mass spectrometer. Additionally, the

Hibbert's ketones released by the hydrolysis of EE were observed in the mass spectrometry data.

	GG	VG
Dimer (m/z)	622	668
EE (m+H/z)	303	317
Second dehydration of model compound (m+H/z)	285	299
VE (m+H/z)	273	287
Hibbert's Ketones (m+H/z)	197	211

Table 5.1: Identified m/z or m+H/z values from LC/MS data.

Two intermediates, EE and VE, were purified through silica column chromatography to make calibration curves for HPLC analysis. The [E] and [Z] isomers of VE could not be separated from each other, so the isomers were assumed to have the same UV cross section. Only the [Z] isomer of EE was produced in significant quantities, as reported [19]. The yields of these intermediates under various reaction conditions are tabulated in Table 5.2. In comparing the ILs, VE is generally not observed in the HMIMCl and HMIMBr ILs, while EE is not observed in the $HMIMBF_4$. In the hydrogen sulfate based ILs, both EE and VE are seen as intermediates. EE was observed in such small quantities for 20 min of reaction because most of it had already reacted to form guaiacol and Hibbert's ketones. The intermediacy of EE is demonstrated by the 5-min reaction data in Table 5.2. The higher yield of VE at high temperatures as compared to the yield of EE demonstrates the relative reactivity of each intermediate under the reaction conditions. In previous work by Jia et al., the EE yield in 110°C HMIMCl was tracked more extensively to show the yield reaching a maximum as the EE was formed

and subsequently hydrolyzed over the first few minutes of the reaction [26]. The other intermediates, including the dimer, form in significant quantities and continue to break down to form guaiacol. These intermediates were not tracked quantitatively herein, although the degradation of the dimer should follow the same path as the monomer.

	110°C*		110°C		130°C		150°C	
IL	VE	EE	VE	EE	VE	EE	VE	EE
HMIMCl	0	5.4	0	trace	0	trace	0	0
HMIMBr	0	1.4	0	trace	trace	0	0	0
$BMIMHSO_4$	1.3	trace	6.0	trace	6.3	trace	2.1	0
$HMIMHSO_4$	0	0	2.4	trace	2.8	0	3.3	0
$HMIMBF_4$	2.1	0	3.6	0	17.4	0	22.9	0

Table 5.2: Yield of VE and EE intermediates (* indicates 5 min reaction time, all others are 20 min reactions)

To further compare the acidic ILs, VG was employed as the lignin model compound at 150 °C. At this temperature, VG and GG displayed the same trends in guaiacol yield (Figure 5.2). Mass spectrometry data also indicated that the other degradation products and intermediates of VG were the methylated analogues of the GG products and intermediates (Table 5.1). These results suggest that the phenolic hydrogen is not involved in the pathways that break the β-O-4 ether linkage.

Multiple reaction times were used to compare the different ILs at 150°C. As can be seen in Figure 5.3, the identity of the IL strongly affects the rate of guaiacol production from GG. Overall, these results illustrate that most of the guaiacol is released over the first 20 minutes of the reaction in the case of HMIMCl, HMIMBr, and $BMIMHSO_4$, while the $HMIMBF_4$ and $HMIMHSO_4$ react more slowly. Interestingly, the yield of guaiacol reaches its maximum and levels off much earlier when HMIMBr is used

than in any of the other ILs. The difference in selectivity between the ILs can be attributed to the different intermediates formed in the reactions. EE tends to be less stable than VE, so ILs that promote the formation of EE over VE tend to produce higher yields of guaiacol. Noise in the data in Figure 5.3 can be attributed to small inaccuracies in the mass balance and pipettes that are compounded by the small reactor volume.

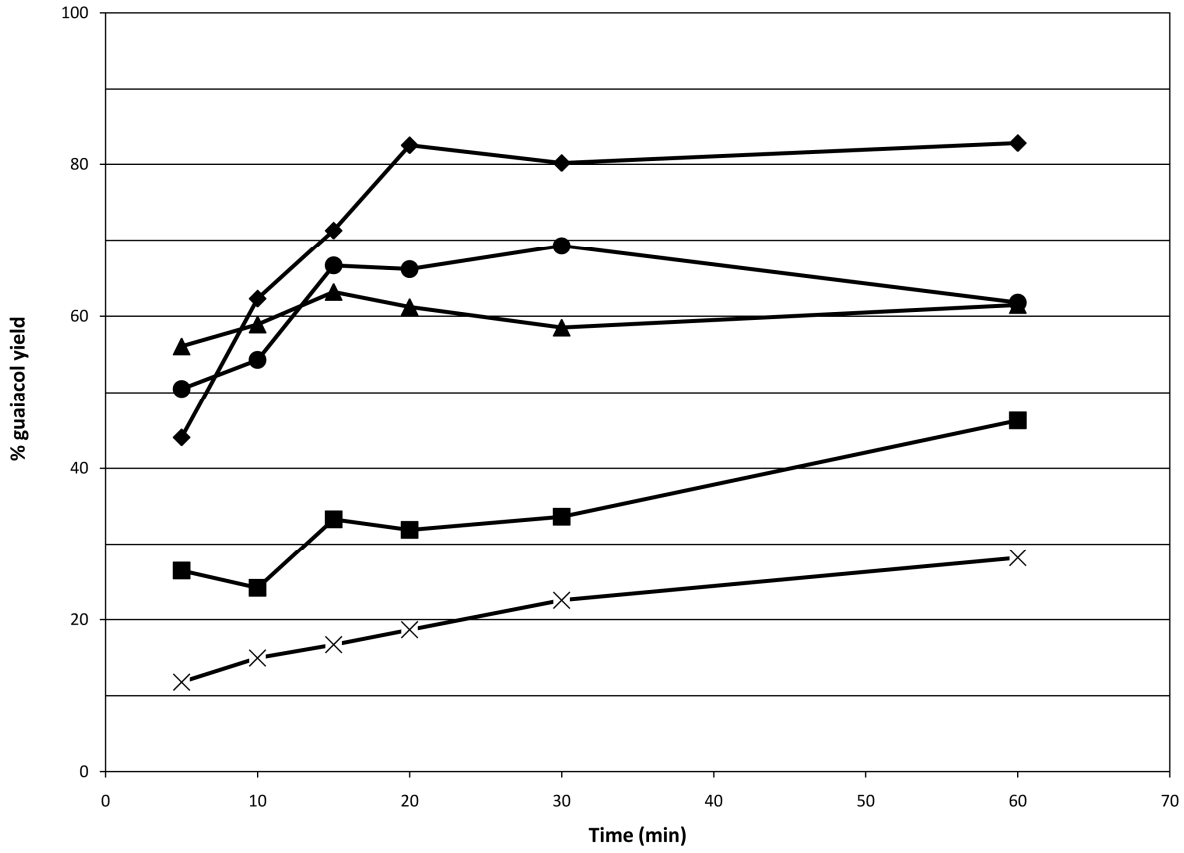
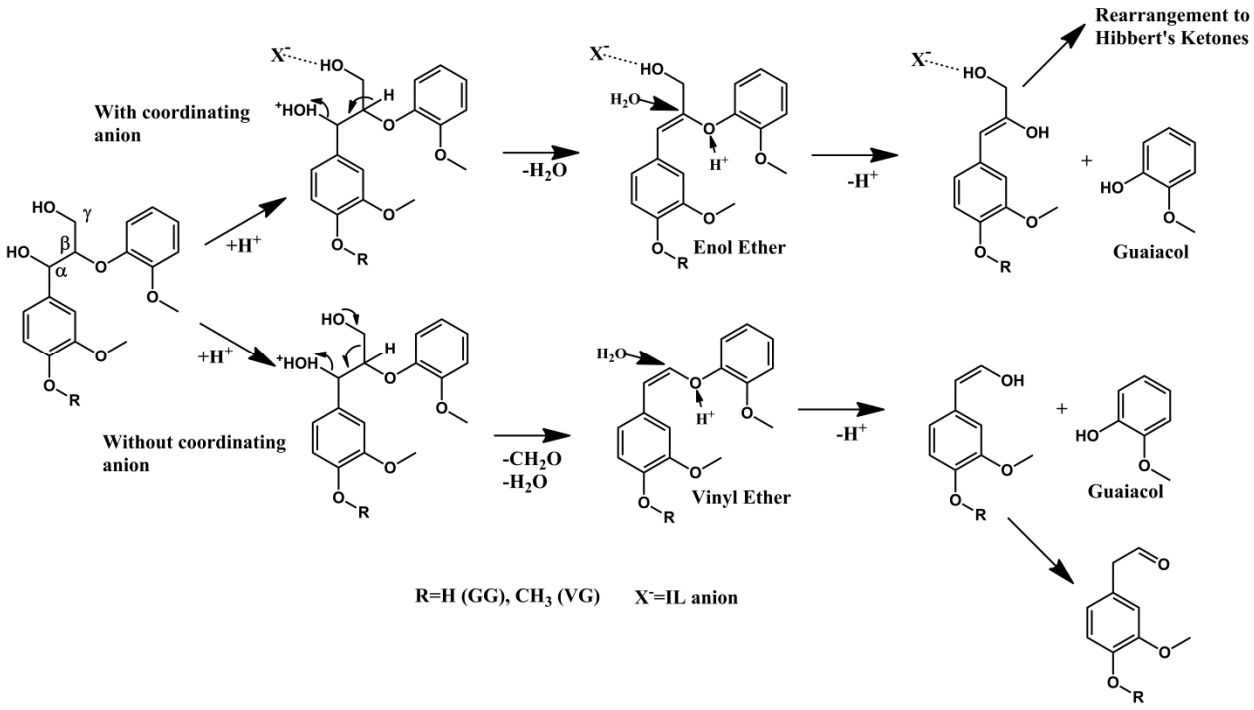


Figure 5.3: Guaiacol yield from GG in HMIMCl (♦), HMIMBr (▲), $BMIMHSO_4$ (●), $HMIMHSO_4$ (■), and $HMIMBF_4$ (×) at 150°C over the course of 60 min.

5.3.3 Discussion

Based on the acidity measurements, the relative acidity of the ILs is as follows: HMIMCl>HMIMBF$_4$> HMIMHSO$_4$≈HMIMBr≈BMIMHSO$_4$. Even though there is a difference between the acidity of each IL, the difference is not very large. At 150°C, the relative guaiacol yield produced by each IL is: HMIMCl>BMIMHSO$_4$>HMIMBr>HMIMHSO$_4$>HMIMBF$_4$. While the most acidic IL is the best performing, the reactivity of the rest of the ILs does not follow the trend in their acidity. It is apparent, therefore, that the acidity of the IL is not the only influence in how readily the β-O-4 ether bond is broken by acidic ILs.

With the exception of BMIMHSO$_4$ the only difference between the ILs is the anion. This indicates the difference in reactivity likely stems from the difference in anions that are present during the reaction. The most likely explanation comes from the ability of the anion to interact with the alcohol groups on the model compounds through hydrogen bonding. As demonstrated in Scheme 5.1, the anion's coordination with the alcohol groups is likely important in stabilizing the necessary intermediates that facilitate guaiacol formation and the cleavage of the β-O-4 ether bond.



Scheme 5.1: Pathways of GG and VG degradation in acidic ILs. Analogous chemistry occurs with GG and VG dimers.

The hydrogen bond basicity of all of these anions has been measured both in conventional salt solutions and in ionic liquids. In both cases, the relative strength of the hydrogen bonding is: $Cl^- > Br^- > HSO_4^- > BF_4^-$ [32], [33][32][33]. It has also been shown that, when dissolving lignocellulosic biomass, the hydrogen bond basicity and the size of the anion play an important role in disrupting the structure of the biopolymers. As predicted by the hydrogen bonding basicity measurements, the ability of an ionic liquid to dissolve biomass follows the series: $Cl^- > Br^- > BF_4^-$ (HSO_4^- based ILs were not tested) [34]. Reactivity of the HMIM-based ILs with the lignin model compounds follows the same trend as the relative hydrogen bond basicity of the anions of the IL.

Evidence of this coordination can be found in the reaction results. For instance, $HMIMBF_4$ tends to form a large quantity of VE. This is observed to a lesser extent in the $BMIMHSO_4$ and $HMIMHSO_4$ IL. In order for VE to form, the γ-hydroxyl group must deprotonate and the γ-carbon must break off to form formaldehyde [6] Scheme 5.1 demonstrates that, in the case of chloride, bromide, and hydrogen sulfate based ILs, the anion could stabilize the hydroxyl group and prevent deprotonation through coordination. Only the less coordinating anions allow significant amounts of VE to form. This reaction scheme should be similar for GG, VG and dimers formed through the condensation of two GG or VG monomers; the dimers should contain structures analogous to EE and VE depending on the coordinating anions present in the reaction mixture. The presence of these dimer intermediates also explains the continued formation of guaiacol even after EE and VE have been exhausted.

5.4 CONCLUSION

Acidic ILs are successful at breaking down lignin model compounds by hydrolyzing the β-O-4 ether linkage. While the acidic environment of the IL is what catalyzes the hydrolysis reaction, the anions present with the IL have a significant effect on the yield. The approximate Hammett acidity of all the ILs was between 1.48 and 2.08, although the relative acidity of the ILs did not correlate with their reactivity with the model compounds. Additionally, the intermediates that were observed depended heavily on the anion present in the IL. Consequently, we posit that the ability of the anion to hydrogen bond with the model compound is a major contributor to the ability of an acidic

IL to effectively catalyze hydrolysis of the β-O-4 ether linkage with stronger coordination leading to a chemical environment more conducive to ether bond hydrolysis.

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Chapter 6: Depolymerization of oak wood lignin under mild conditions using the acidic ionic liquid 1-H-3-methylimidazolium chloride*

6.1 INTRODUCTION

As the demand for alternatives to petroleum based resources continues to grow, new and better methods must be developed to utilize "green" energy sources [1]. Biomass has been indicated as a major renewable resource that will continue to be developed in future generation energy production, with an annual yield of 1.37 billion dry tons in the United States [2]. In order to gain full access to these biomass resources through enzymatic or biological processing, the raw biomass must be pretreated to disrupt structure and remove lignin [3]. Lignin is one of the three biopolymers that comprise plant biomass; 15-30% is lignin, with the balance being cellulose and hemicellulose. On an energy basis, lignin comprises about 40% of plant biomass [4–6].

Ionic liquids (ILs) are a class of chemicals that are generally composed of an organic cation with an inorganic counter ion and melt at or below 100°C. Because of their ionic nature, ILs have essentially no vapor pressure, which can facilitate separations. By choosing appropriate ion pairs, properties such as solubility, thermal and chemical stability, and viscosity can be tuned [7], [8]. Ionic liquids are often considered a green solvent due to advantages in separations and reusability. ILs have also received attention in the field of biomass processing because of their ability to solubilize cellulosic biomass [9–11]. Acidic ILs can also be used as both solvent and catalyst. Studies utilizing model

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compounds that replicate the structures in lignin have shown that these acidic ILs are effective for the hydrolysis of the β-O-4 ether linkage, a common structure in lignin (Jia et al., 2010a; Cox et al., 2011).

Lignin is a complex, amorphous biopolymer that is incorporated into the cell wall in plant matter. While cellulose and hemicellulose are polysaccharides, lignin is comprised of phenyl-propanoid units that are linked through enzymatic dehydrogenative polymerization of hydroxy- and methoxy- substituted cinnamyl alcohols [6], [14]. There are many different linkages formed by this polymerization, such as 5-5, α-O-4, β-O-4, and β-5 [15]. The β-O-4 linkage is the most common, accounting for 45-50% of the linkages in softwood lignin [16]. The complex, amorphous structure of lignin is very resistant to biological attack, and only metabolized by a few species in nature [17]. This recalcitrance is one of the major defenses that plants employ against attack in nature. Unfortunately, lignin is also a major hurdle for the effective utilization of biomass as a fuel and chemical feed stock because it retards chemical and biological attack [18].

Currently, there are a few methods used to process biomass [2], [15], [19], [20]. In the pulp and paper industry, bases [21], acids [22], and organic solvents [23] have been used to separate lignin from cellulosic biomass. In the field of biofuel production, methods such as gasification, fast pyrolysis, and biological digestion have produced biofuels and commodity chemicals [24–26]. Pretreatment is often an important step in the effective utilization of biomass. Some work has already been done using steam explosion, ammonia fiber expansion, acid hydrolysis, and even ionic liquids in the pretreatment of lignocellulosic biomass to provide a more accessible structure for

biological attack [3], [27], [28]. The work presented herein seeks to add to this body of pretreatment research by focusing on lignin degradation.

Lignin can be degraded through a number of different chemical paths (Gierer, 1980; McDonough, 1992; Jia et al., 2010b; Jia et al., 2011). One such path utilizes an acid catalyst that leads to the hydrolysis of ether linkages. The depolymerization begins with the protonation and dehydration of an alkyl hydroxyl group, which leads to either an enol ether or vinyl ether intermediate. The ether linkage is then hydrolyzed followed by a rearrangement to form a Hibbert's ketone [23], [31]. Model compounds are commonly used to study the hydrolysis reactions; studies with the lignin model compounds, guaiacylglycerol-β-guaiacyl ether and veratrylglycerol-β-guaiacyl, revealed the same protonation/dehydration/ hydrolysis pathway when an acidic IL is used as both the solvent and the catalyst (Jia et al., 2010a; Cox et al., 2011). The pathway of this reaction in acidic ILs has been shown to be dependent on the ability of the anion to hydrogen bond with the lignin model compound [13]. In this study, we investigate the ability of 1-H-3-methylimidazolium chloride (HMIMCl), an acidic IL, to depolymerize lignin as a route to the effective pretreatment of biomass with HMIMCl.

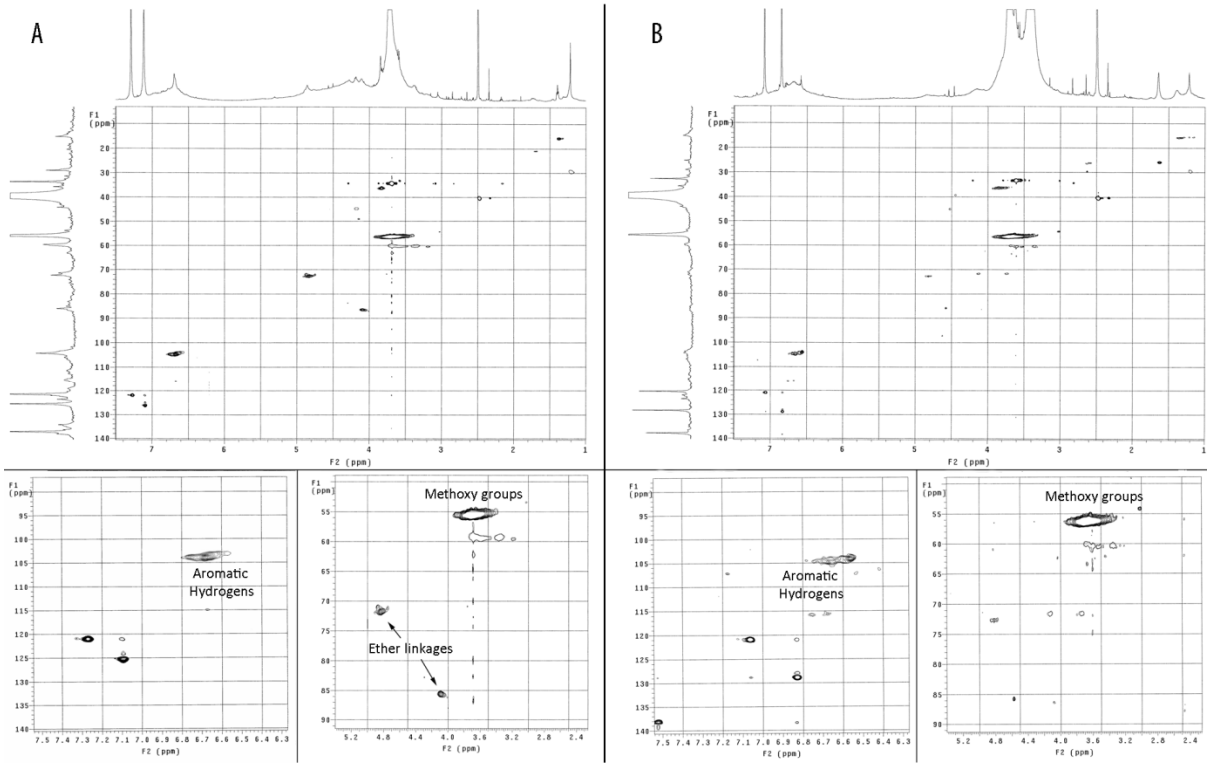

Figure 6.1: 2D HSQC NMR data for lignin A) without depolymerization and B) after depolymerization in HMIMCl at 150°C for 1hr. The abscissa is represents the data from H^1 NMR, while the ordinate is the data from C^{13} NMR. Detailed views of two sections of interest are displayed below the full plot of the data.

6.2 EXPERIMENTAL

6.2.1 Material

1-H-3-methylimidazolium chloride (HMIMCl) (>95%), 1-ethyl-3-methylimidazolium acetate (EMIMOAc) (>90%), 1-ethyl-3-methylimidazolium chloride (>95%), dextran standard 12000, and dextran standard 5000 were purchased from Sigma Aldrich and used without further purification unless otherwise noted. Acetone (99.8%), toluene (99.9%), ethyl acetate (99.9%), 2-naphthol (98%), dimethyl sulfoxide (DMSO)

(99.97%), dimethyl formamide (99.92%) dimethyl sulfoxide-d_6 (99.9%), light mineral oil, phosphoric acid (purity not given, labeled "pure"), lithium bromide (99%) and sodium hydroxide (98.7%) were purchased from Fisher Scientific and used without further purification unless otherwise noted.

Lignin was extracted from wood through the modified method developed by Sun, et al. [9]. Scrap oak wood was ground to a powder using a pneumatic powered abrasive disk. In a typical extraction, 2 g of wood dust was dissolved in 25 g of EMIMOAc by stirring at 110°C for 48 hr. The stirring mixture was held under vacuum until the pressure stabilized below 100mTorr to remove any incidental water. Once the 48 hr had elapsed, 400 ml of a 1:1 mixture of acetone and water was added and stirred for at least 3 hr or until there were no more remaining biomass/IL clumps. The mixture was filtered and the precipitated cellulose discarded. The acetone in the remaining homogenous solution was evaporated under mild heating (50-75°C) and vacuum. The precipitated lignin was then filtered from the solution, washed three times with distilled water, and dried under vacuum. The water was evaporated from the EMIMOAc, which was subsequently washed twice with 20 ml of toluene and twice with 20 ml of ethyl acetate. The IL, which maintained a dark brown color, was dried on a Schlenk line and reused in the next lignin extraction. Typical lignin recovery was about 150 mg. The structure of the lignin was verified by comparing the 2D heteronuclear single quantum coherence NMR (2D HSQC NMR) data (Figure 6.1A) with published NMR measurements [32], [33]. No peaks resembling structural carbohydrates were observed when the NMR results were compared to 2D HSQC NMR for cellulose triacetate [32].

6.2.2 Experimental procedures

In a typical lignin depolymerization experiment, 10 mg of lignin and 2.5 µl of water was deposited into a 300 µl reaction vial. HMIMCl was melted in a boiling water bath and 300 µl was transferred to the reaction vial via pipette. In the case of the 2-naphthol experiments, 4.5 mg of 2-naphthol was added to the vial as well. The vial was then placed into a Thermo Scientific Reacti-Therm heated/stirred module. The reaction was carried out at the prescribed temperature. Once the required time had elapsed, the reaction mixture was quenched in 1 ml of the eluent used for gel permeation chromatography (GPC) (80:20 mixture of DMSO and DMF that contained 20 mM phosphoric acid and lithium bromide). The samples were analyzed on a GPC using a Wyatt Optilab T-rEX differential refractometer detector, two Phenomenex Phenogel 5 µm, 300 mm x 7.8 mm linear columns held at 50°C, and a Waters 515 HPLC pump set at 0.6 ml/min using an 80:20 mixture of DMSO and DMF that contained 20 mM phosphoric acid and lithium bromide as an eluent.

For infrared spectroscopy (IR) and NMR analysis, lignin depolymerization products needed to be separated from the HMIMCl after the reaction. In a typical HMIMCl removal procedure for a 300 µl experiment, the mass of add IL was recorded and the reaction mixture was quenched in 4 ml of water and added to a separatory funnel with 10 ml toluene. Roughly 170 mg of NaOH was dissolved in 10 ml water. Enough NaOH solution was slowly added to the quenched reaction mixture with occasional gentle agitation to introduce an equimolar amount of base to acidic IL. The resulting methylimidazole was extracted with three more rounds of 10 ml toluene. Only gentle

agitation was used to prevent an emulsion from forming. The remaining water was removed from the aqueous phase using gentle heat and vacuum. The product, a mixture of depolymerized lignin and sodium chloride, was then powdered with a mortar and pestle for use in NMR or IR experiments. The structure of lignin was unchanged through this process, as verified by C-NMR and H-NMR.

NMR measurements were made on a Varian Direct Drive 600 MHz NMR spectrometer. For NMR samples, the amount of IL was quadrupled and eight times the standard mass of lignin was used. Experiments were run at 150°C for 60 min. Samples were prepared using the method above for removal of HMIMCl from lignin samples, but scaled for the larger batch size. To make the NMR sample, the powder of sodium chloride and lignin was mixed with 1.3 ml DMSO-d_6. The sodium chloride was filtered from the solution using a pipette packed with a small amount of Kimwipe®. In the case of unreacted lignin, the lignin samples were suspended in 4ml water and 300µl HMIMCl. This suspension then underwent the IL removal procedure to ensure that any differences observed between the reacted and unreacted lignin was caused by the depolymerization and not the extraction process.

IR samples were made by following the standard reaction and IL separation procedures for a 150°C, 60 min reaction. As with the NMR samples, unreacted lignin was subjected to the same IL separation process as the reaction mixture. Because solutions in DMSO were too dilute for IR analysis, the powder of sodium chloride and lignin was suspended in 500 µl of mineral oil. Measurements of the suspended powder

were made on a Thermo-Mattson Infinity Gold FT-IR spectrometer using a liquid cell with sodium chloride windows and a 0.1 mm path length.

6.3 Results and Discussion

Lignin was reacted in HMIMCl under the prescribed conditions and then analyzed using GPC as described in Section 2.2. The results, shown in Figure 6.2, demonstrate that the size of the lignin molecules is being decreased when reacted in the HMIMCl under mild heat. Figure 6.2A is the result of 12k dextran ($\bar{M}_w$=11600, $\bar{M}_n$=8110) and 5k dextran ($\bar{M}_w$=5220, $\bar{M}_n$=3260) standards run on the GPC as comparison for the lignin. Figures 6.2B, C and D are the GPC results from lignin depolymerization experiments run at 110°C, 130°C and 150°C, respectively. In each of the lignin depolymerization GPC results, the curves from left to right represent unreacted lignin, 15, 30, 45, 60, 120, and 180 min reaction, respectively, unless otherwise noted.

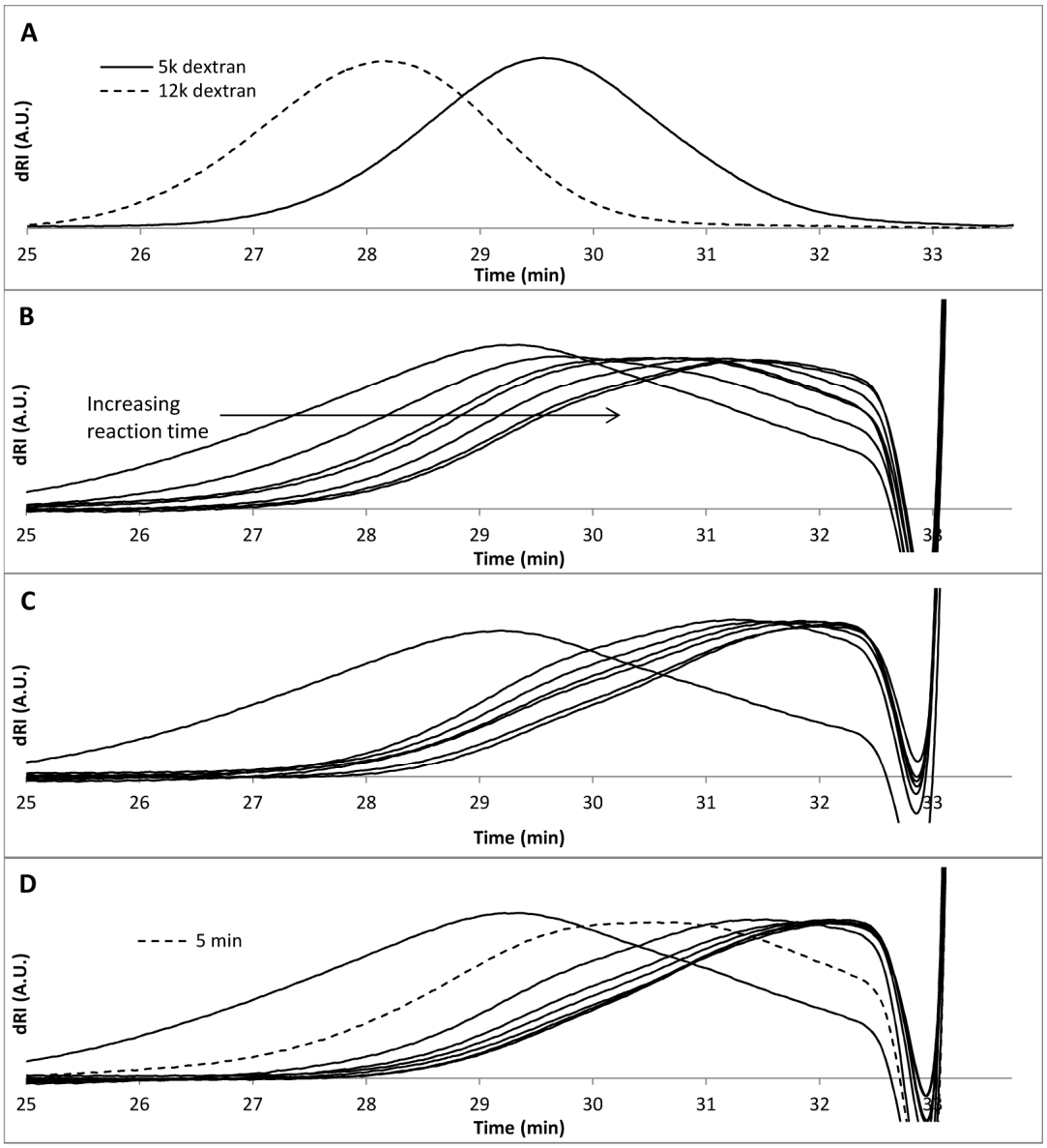

Figure 6.2: GPC data that showing A) both dextran standards, B) the reaction of lignin in HMIMCl at 110°C, C) the reaction of lignin in HMIMCl at 130°C, and D) the reaction of lignin in HMIMCl at 150°C. Curves in B, C, and D show data for a reaction time of 0min, 15min, 30min, 45min, 60min, 120min, and 180min from left to right, respectively. HMIMCl begins to elute between 32 and 33min.

Provided the ether hydrolysis found with model compound studies occurs with lignin (Jia et al., 2010a; Cox et al., 2011), the acidic IL should cause a decrease in molecular size of the lignin by a depolymerization of the lignin macromolecule. As a comparison, the dextran standards were run in the GPC under the same conditions. These dextran samples are significantly different from lignin chemically, so the results do not demonstrate a direct molecular weight comparison. The results from the standards do, however, provide a reference for the size of the lignin molecules over the course of depolymerization. As shown in Figure 6.2, the size of the unreacted lignin is comparable, if not slightly larger than the 5k dextran standard and has a wider range of sizes. It should also be noted that the HMIMCl elutes in the GPC just after 32 min and any lignin fragments eluting past this time would be too small for the GPC column to effectively separate them.

By comparing Figure 6.2B, C, and D, it can be seen that depolymerization proceeds faster and more completely under higher temperatures. At 110°C, the lignin continues to depolymerize throughout the entire three hour reaction period. The 130°C experiment demonstrates a faster reaction. Both the 110°C and 130°C reactions slow down considerably at the end of the reaction period, but do not appear to have reached the limit of depolymerization as the 120 min and 180 min curves in both cases are not superimposed. At 150°C, however, the final two samples at 120 min and 180 min produce curves that are almost identical. The data from a 5 min reaction at 150°C are also included, although a sample at such a short time may make heat transfer into the reaction vial at the beginning of the experiment an issue. The final lignin fragments

eluted over a range centered between the 5k dextran standard and the IL, indicating a significant decrease in molecular size.

In work done with model compounds, the acid catalyzed cleavage of the β-O-4 ether linkage in lignin was found to be a hydrolysis reaction and thus inhibited under dry conditions (Jia et al., 2010a). Figure 6.3A shows the GPC data from experiments at 110°C in which the system was kept dry and an experiment with water present for the sake of comparison. The results of this experiment clearly show that when water is not present, the reaction is inhibited almost to the point of stopping completely. In model compound studies, the first step to cleavage of the β-O-4 ether linkage was the dehydration of guaiacylglycerol-β-guaiacyl ether and veratrylglycerol-β-guaiacyl ether. This prevents the depolymerization reaction from being fully arrested by lack of water because the lignin itself is a source of water for the subsequent hydrolysis of the ether linkages. It should be noted that it is possible that the dehydration reaction could also take place in the process used to extract the lignin from the oak dust. This would reduce the ability of the lignin to dehydrate and subsequently hydrolyze under dry conditions. Such an effect could contribute to the minimal depolymerization seen in Figure 6.3A.

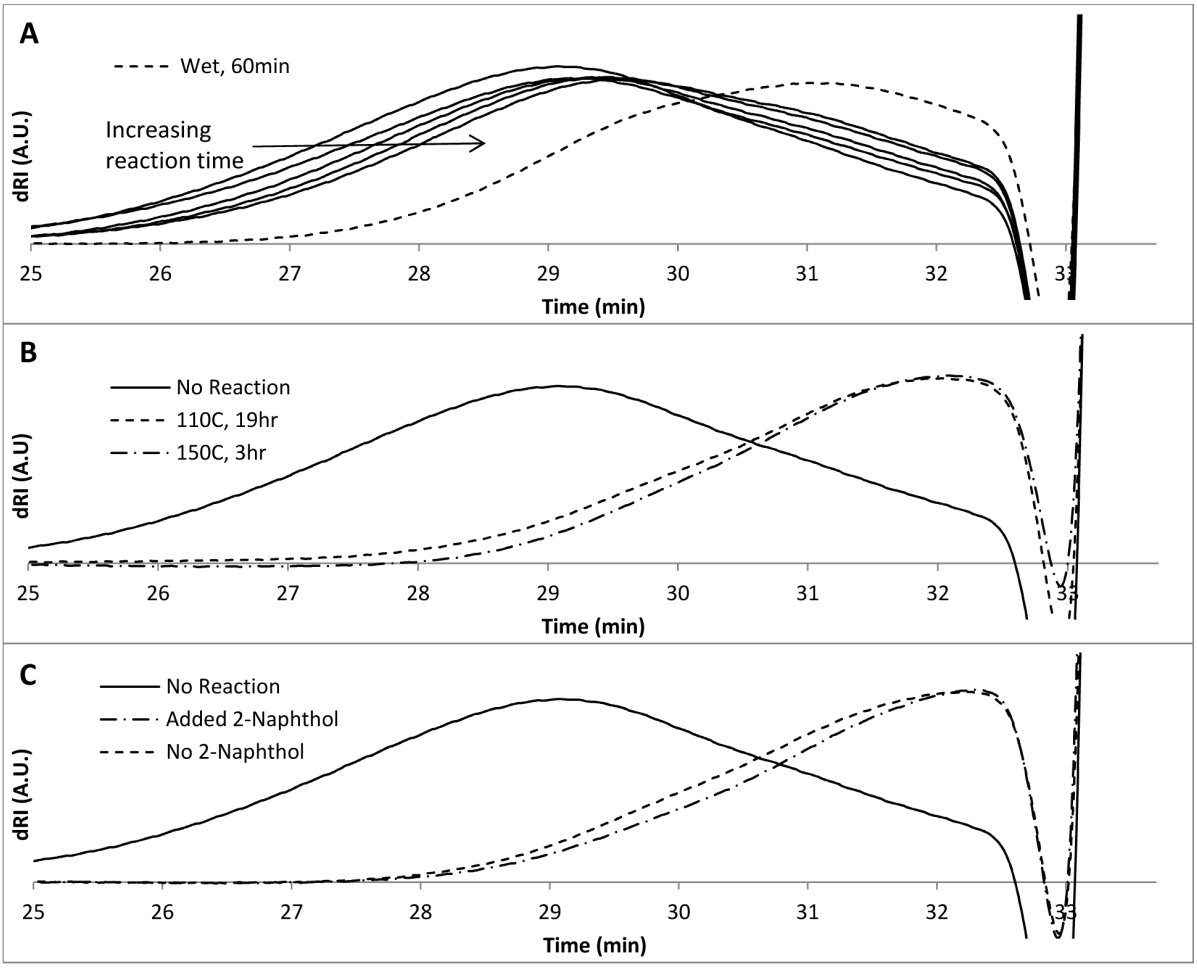

Figure 6.3: GPC data showing A) the reaction of lignin in HMIMCl at 110°C under dry conditions, B) the reaction of lignin at 110°C carried to completion, and C) the result of adding 2-naphthol to the reaction of lignin in HMIMCl at 150°C.

Because only the experiments at 150°C seemed to react to completion, experiments were run to find the end point of the lower temperature reactions. Figure 6.3B shows the results of allowing lignin to react in HMIMCl for 19 hr at 110°C along with the GPC data from lignin reacted for 180 min at 150°C. It appears that, after an extended period of time, the lower temperature reaction reaches a similar end point to the

higher temperature reaction. This indicates that the differences between the depolymerization at the different temperatures tested are most likely based on differences in reaction rates and not in the presence of different mechanisms at different temperatures.

It has been observed that one of the major inhibitors to lignin depolymerization is the repolymerization of lignin fragments [23], [31]. The most common reaction for this repolymerization is alky-aryl radical coupling [23], [34]. As a test to see the extent to which repolymerization is important in the acidic IL-lignin system, 2-naphthol was added to the reaction mixture as a radical scavenger [34]. The GPC data from this experiment, carried out at 150°C for 60 min, are shown in Figure 6.3C. 2-Naphthol appears to increase the degree of depolymerization, indicating that there is some amount of radical repolymerization occurring in the system. Control experiments carried out using 1-ethyl-3-methylimidazolium chloride (not shown) confirmed that 2-naphthol does not, on its own, cause lignin depolymerization. This result helps to confirm that the depolymerization reaction observed in this system occurs through the same pathways as observed in model compound studies and elsewhere in the literature (McDonough, 1992; Jia et al., 2010a; Yokoyama and Matsumoto, 2010).

As a method to apply a numerical comparison to the depolymerization end points of the reaction under different conditions, a Gaussian distribution curve was fit to the data and then normalized. The fit was qualitatively good, although a significant portion of the curve associated with the depolymerized lignin is extrapolated. Assuming the depolymerized lignin curve maintains a roughly Gaussian shape past the elution of

HMIMCl and the refractive index response of depolymerized lignin is the same as the lignin pre-reaction, this analysis will provide a means of comparing depolymerization end points. After 180 min at 150°C, the peak elution shifted by 2.8 min and there was a 44% overlap between the pre- and post-reaction curves. In the case of the 19 hr reaction at 110°C, the peak shift was 3.2 min and a peak overlap of 40%, which indicates a slightly higher degree of depolymerization than the 150°C reaction. When 2-naphthol was added to the mixture reacted at 150°C for 120 hr, the peak shift was 3.8 min and the peak overlap was 32%. This confirms that the 2-naphthol allows for more complete depolymerization through the inhibition of radical coupling of lignin fragments.

In an effort to further verify the mechanisms present in this reaction, 2D HSQC NMR was used to observe the change in lignin structure when reacted in HMIMCl. This technique measures the coupling between carbon and hydrogen resonance and thus shows peaks for structures that contain an H-C bond [32], [35]. Lignin before and after depolymerization was removed from the acidic IL and analyzed using this NMR technique. The results of this analysis, shown in Figure 6.1, demonstrate the near complete disappearance of the ether linkages present in the lignin. As a baseline for comparison, the methoxy group peak should not change over the course of the reaction. This shows that the ether linkages are cleaved over the course of the reaction. In addition to disappearance of the ether linkages, the signal from the aromatic H-C structures diminishes. This is evidence of radical coupling involving the aromatic rings. The peaks that are further downfield from the aromatic signal are associated with hydrogen bonded

to double bonded carbon. The change in these peaks may indicate the presence of Hibbert ketones, as observed in the literature (McDonough, 1992; Jia, et al., 2010a).

In addition to 2D HSQC NMR, IR spectroscopy was used to characterize the change in lignin structure over the course of depolymerization. In order to provide a direct comparison, the size of the aromatic C-C bond peak was equalized between the two measurements. Then, the peaks associated with the C-O bonds in the ether linkages were compared. Due to the nature of the procedure to remove lignin from the HMIMCl after the reaction, the IR samples were comprised of a powder suspended in mineral oil because dissolution in DMSO resulted in too much interference from the solvent for measurement of lignin. The procedure for removing HMIMCl after the reaction necessitated that the powdered samples were a mixture of lignin and sodium chloride, which diminished the IR absorbance of the lignin through dilution. Figure 6.4 shows representative IR data comparing lignin before and after depolymerization at 150°C for 60 min. One of the peaks associated with the ether linkages decreases after the reaction, which is consistent with hydrolysis of the β-O-4 ether linkage. The other ether peak located at 1100 cm^{-1} is associated with the methoxy groups in the lignin, which are not affected by the acid catalyzed depolymerization reaction. Because of the noisy quality of the data, the experiment was run multiple times, each time with the same result.

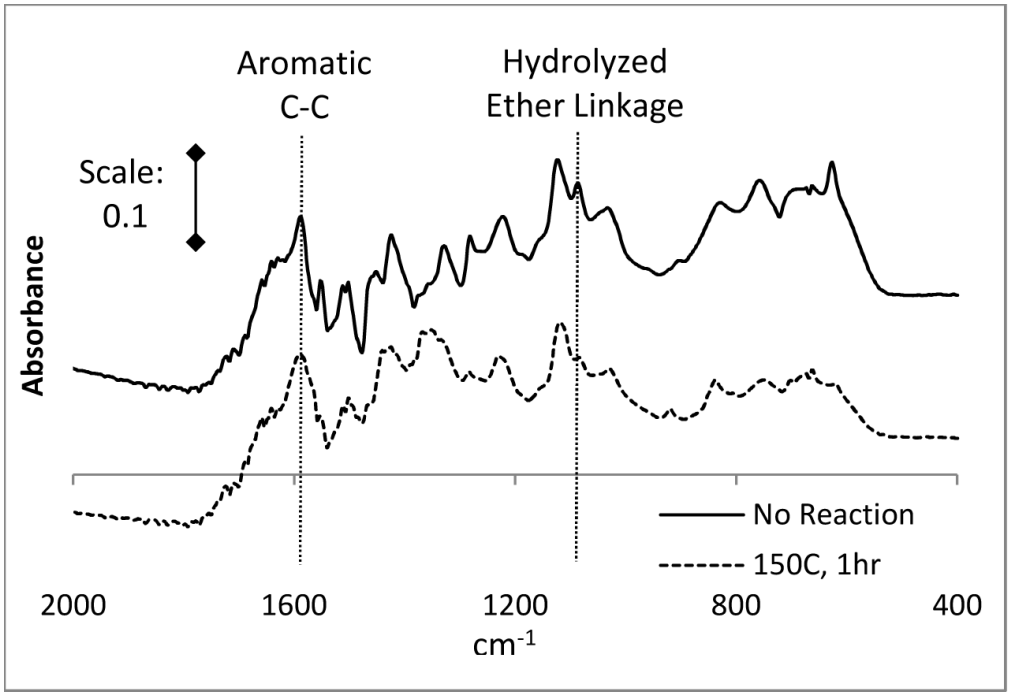

Figure 6.4: IR data of lignin before and after depolymerization in HMIMCl at 150°C for 60min. The post-reaction data was adjusted by 25% to equalize the aromatic C-C peak.

6.4 CONCLUSIONS

Acidic IL HMIMCl is an effective combination solvent/catalyst for the depolymerization of lignin. Between 110°C and 150°C, increasing temperature increases the rate of reaction, although the ultimate end point of the depolymerization remains roughly the same. Lignin depolymerization in HMIMCl proceeds via a hydrolysis reaction that attacks alkyl-aryl ether linkages. Insight gained from this study suggests a pretreatment method that combines the biomass solubilizing abilities of ILs with catalytic depolymerization of lignin. Whereas previous pretreatment research focused on only the structure disrupting abilities of ILs, this work points to a method that would provide both structural and chemical pretreatment.

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Chapter 7: Pretreatment of yellow pine in an acidic ionic liquid: Extraction of hemicellulose and lignin to facilitate enzymatic saccharification

7.1 Introduction

The depletion of petroleum resources and the specter of anthropogenic climate change give an impetus to better utilize renewable sources of energy. With an annual yield of 1.37 billion tons in the US, lignocellulosic biomass has the potential to be a significant source of energy [1]. For this reason, lignocellulose has garnered significant attention as a platform for renewable energy production and a number of technologies have been developed to take advantage of biomass [1], [2]. One such technology is the fermentation of sugars derived from lignocellulose. The most common product of this fermentation is ethanol, although other products such as butanol are reported [3–5]. The US has required that fuel producers utilize 21 billion gallons of non-cornstarch based ethanol in fuel production, a requirement which is could be achieved through fermentation of cellulosically-derived saccharides [6].

A major hurdle in the effective utilization of biomass is lignin. Lignin is a complex biopolymer composed of phenylpropanoid units that acts as an essential glue that holds cellulose fibers together in plant cell walls [2]. The lignin biopolymer is rich in aromatics and is very resistant to biological attack, preventing the biomass from being degraded into saccharides or directly digested microbially [7]. In order to effectively convert lignocellulose into fuel such as ethanol using currently available technology, the

polysaccharides must be converted into monosaccharides that are conducive to microbial digestion. This process is most often achieved through enzymatic saccharification of cellulose through hydrolysis of the glycosidic linkages [8]. For this step to be completed, pretreatment of the biomass must be done to disrupt the structure of the lignocellulose to allow for enzymatic attack of the polysaccharides [8–10]. The pretreatment and saccharification steps are the largest process hurdles in making enzymatic biorefineries economical [9]. Different methods, such as steam explosion, dilute acid hydrolysis, ammonia explosion, and ionic liquid treatment, have been explored to open the biomass structure to allow enzymatic attack [9], [11–14]. Herein, we report a method that effectively pretreats yellow pine wood chips by depolymerizing and extracting the lignin along with the hemicellulose under mild conditions using the acidic ionic liquid 1-H-3-methylimidazolium chloride (HMIMCl) as both solvent and catalyst.

Ionic liquids (ILs) are a class of chemical compounds composed of anions and cations that melt at or below 100°C and have essentially no vapor pressure. By choosing an appropriate anion/cation combination, the properties of ILs, such as viscosity, melting point, solubility, and stability can be tuned [15], [16]. The solvent properties of some ILs allow them to either partially or completely solubilize lignocellulosic biomass [17–19]. Ionic liquids have been investigated as a method for performing various chemistries on cellulose [20], [21]. ILs have also received a significant amount of attention as a method to pretreat biomass through extraction of lignin and disruption of cellulose structure [13], [22–24]. In recent studies, HMIMCl was shown to hydrolyze the ether linkages in phenolic and non-phenolic lignin model compounds and to depolymerize oak wood

lignin under mild conditions, suggesting a facile method for treatment of biomass [25–27]. The study reported herein tests the ability of this acidic IL to pretreat biomass through reactive delignification caused by the acid catalyzed cleavage of the ether linkages in lignin. Efficacy of pretreatment has been verified via enzymatic digestion of pretreated samples into monosaccharides using cellulase enzymes. While there has been research performed using ionic liquids for pretreatment, to the knowledge of the authors, the use of an acidic ionic liquid as a combined solvent and reactive delignification catalyst is a new development in pretreatment research.

7.1 RESULTS AND DISCUSSION

Pretreatment of yellow pine wood chips was carried out as follows: molten HMIMCl (1.0 ml) was added to yellow pine wood chips (30 mg) along with a small amount of water (2.5 μl). The mixture was stirred at 110°C, 130°C, or 150°C for anywhere from 5 to 300 min. The reaction was quenched with a 1:1 acetone and water solution. The cellulose-rich solids from this solution are referred to as Fraction 1. With the exception of the 180 and 300 min treatments at 150°C, which contained high amounts of insoluble char, Fraction 1 maintained the structure of the initial wood chips. When the acetone was evaporated from the solution, the precipitated lignin was collected and is referred to as Fraction 2. The remaining aqueous solution is call Fraction 3. Both solid fractions were dried in a vacuum oven at 60°C for at least 8 hr before further analysis. Fraction 1 was then saccharified with sulfuric acid using the modified method published by the National Renewable Energy Lab (NREL) [28]. Use of acetone to separate the

lignin- and cellulose-rich fractions and sulfuric acid for saccharification are solely for the purpose of analysis and not necessary in the pretreatment process. Figure 7.1 shows the untreated wood and Fraction 1 after 60, 180, and 300 min of treatment at 130°C.

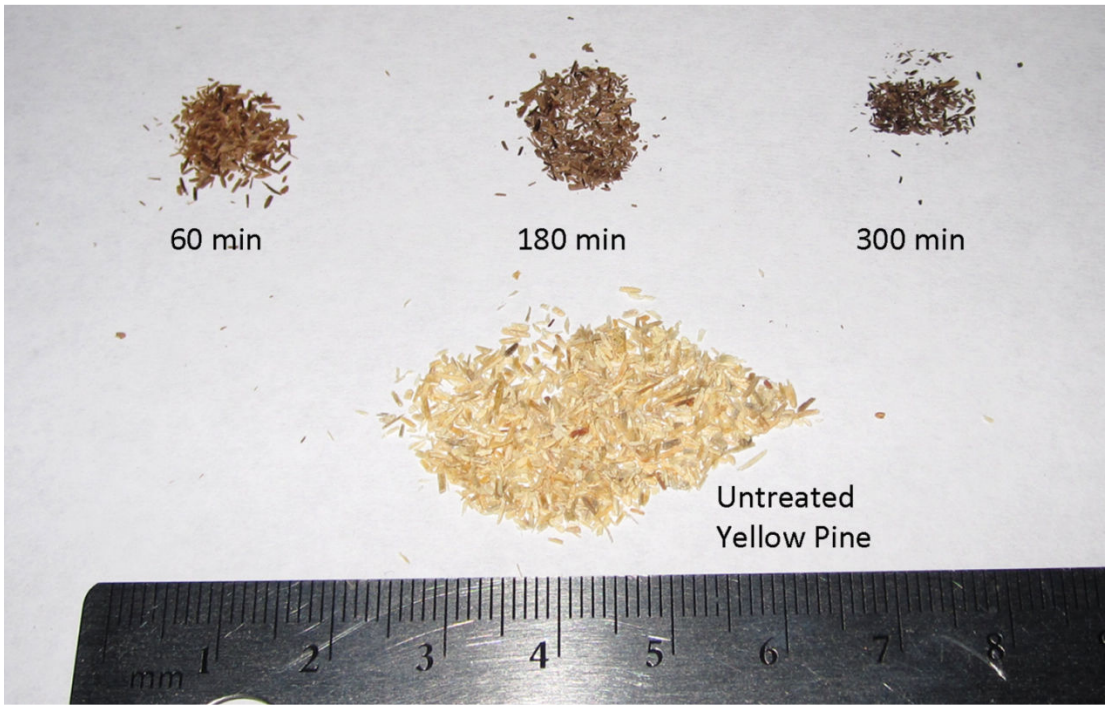

Figure 7.1: An image of untreated yellow pine and Fraction 1 from treatment with HMIMCl at 130°C for 60, 180, and 300 min.

Figure 7.2 shows the fraction of the original mass recovered in Fraction 1 and Fraction 2 based on pretreatment time and temperature. The data show how the HMIMCl treatment removes mass from the remaining insoluble wood chips. Much of this mass was recovered in the lignin-rich Fraction 2. Higher temperatures increase the weight loss from Fraction 1 and increase the recovery in Fraction 2. Based on the repeated experiments at 130°C, the 90% confidence intervals for the normalized mass recovery of Fraction 1 and Fraction 2 are ±0.15 and ±0.04, respectively. Using a modified method

developed by Sun et al., in which lignin is extracted using 1-ethyl-3-methylimidazolium acetate (EMIMAc), a sample of unreacted yellow pine lignin was obtained as a standard [29]. This standard, along with lignin recovered from the HMIMCl treatment was analyzed using H-NMR. The H-NMR data for the standard showed peaks that are consistent with the ether linkages that comprise the most common linkages between phenylpropane units in lignin, while the lignin extracted with HMIMCl treatment did not display any peaks that would correspond to an ether linkage. The NMR peaks were observed at δ=5.7 and 5.3 ppm in the EMIMAc-extracted lignin and most likely corresponding to the H-C-O structure of ether linkages. This result is consistent with previous work demonstrating the ability of acidic ILs, such as HMIMCl to hydrolyze the ether linkages in lignin and lignin model compounds [25], [27]. These results indicate that HMIMCl is dissolving and depolymerizing the lignin from the yellow pine.

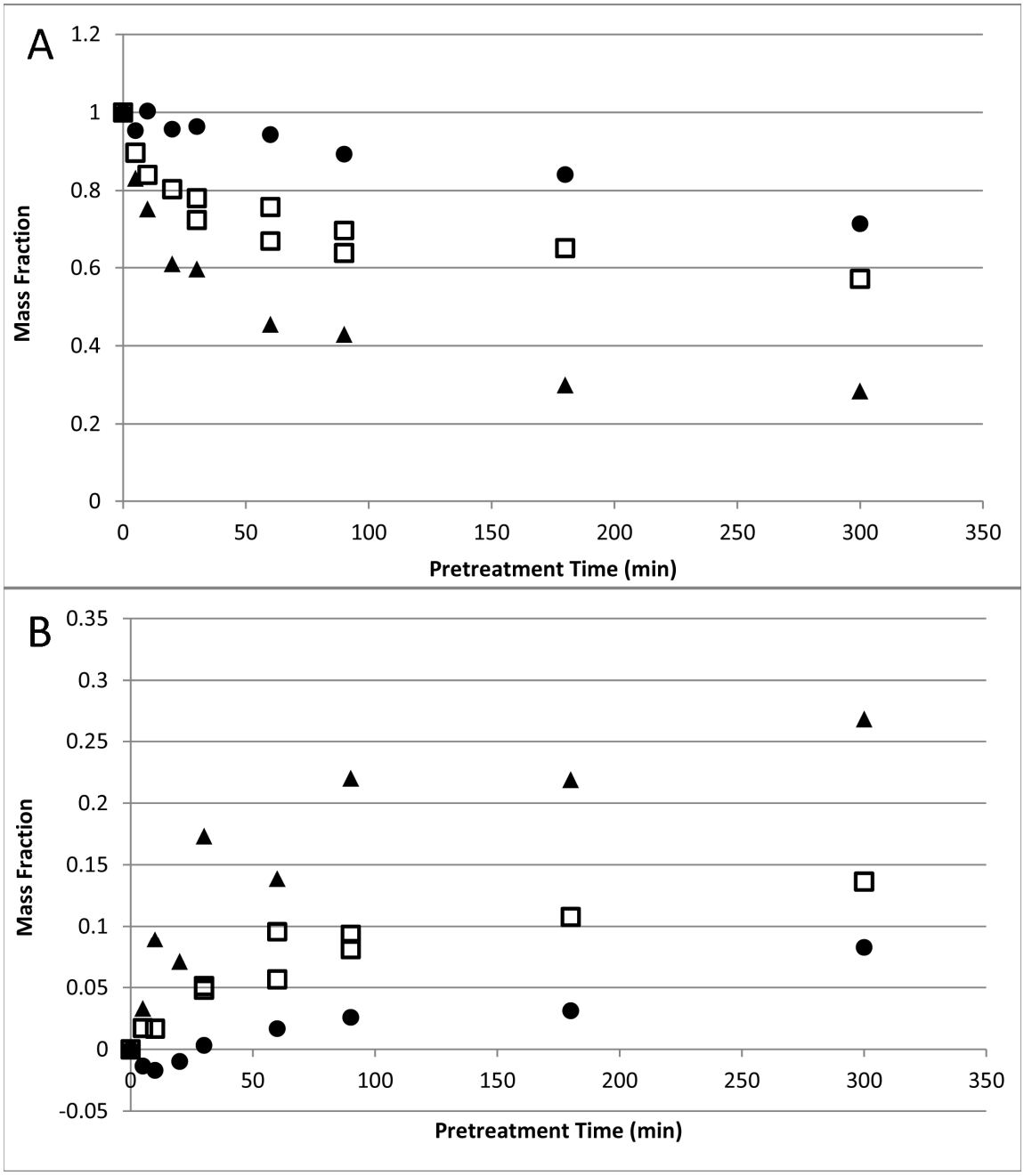

Figure 7.2: Weight recovered in A) Fraction 1 and B) Fraction 2 from pretreatments carried out at 110°C (●), 130°C (□), and 150°C (▲).

Fraction 1 was treated with sulfuric acid to yield a solution of monosaccharides. Analysis of the monosaccharides provides information on the behavior of cellulose and

hemicellulose under HMIMCl pretreatment conditions. Cellulose is a polymer composed of glucose, while yellow pine hemicellulose is primarily composed of mannans [30]. By comparing the recovery of glucose to mannose in Fraction 1, the relative amounts of cellulose and hemicellulose can be inferred. Figure 7.3 shows the recovered glucose and mannose as a fraction of the original mass of the yellow pine sample. The 90% confidence interval for these data is ±0.05, based on repeated experiments at 130°C. The mannose disappears completely if samples are treated long enough at all temperatures tested, which indicates a removal of hemicellulose from the treated wood. Higher temperatures lead to drastically faster hemicellulose removal. The glucose recovery also decreases in 130 and 150°C treatments. This is most likely associated with degradation of the cellulose by the HMIMCl. Additionally, Fraction 1 from the longer 150°C treatments produced significant amounts of char instead of the darkened wood chips recovered in Fraction 1 from 110 and 130°C treatments, which is consistent with conversion of cellulose into char at higher temperatures. Based on the decrease over time of recovered glucose in Fraction 1 treated at 130°C, there is some degradation of cellulose happening in this case as well. 110°C does not appear to be a high enough temperature to cause cellulose degradation in this system.

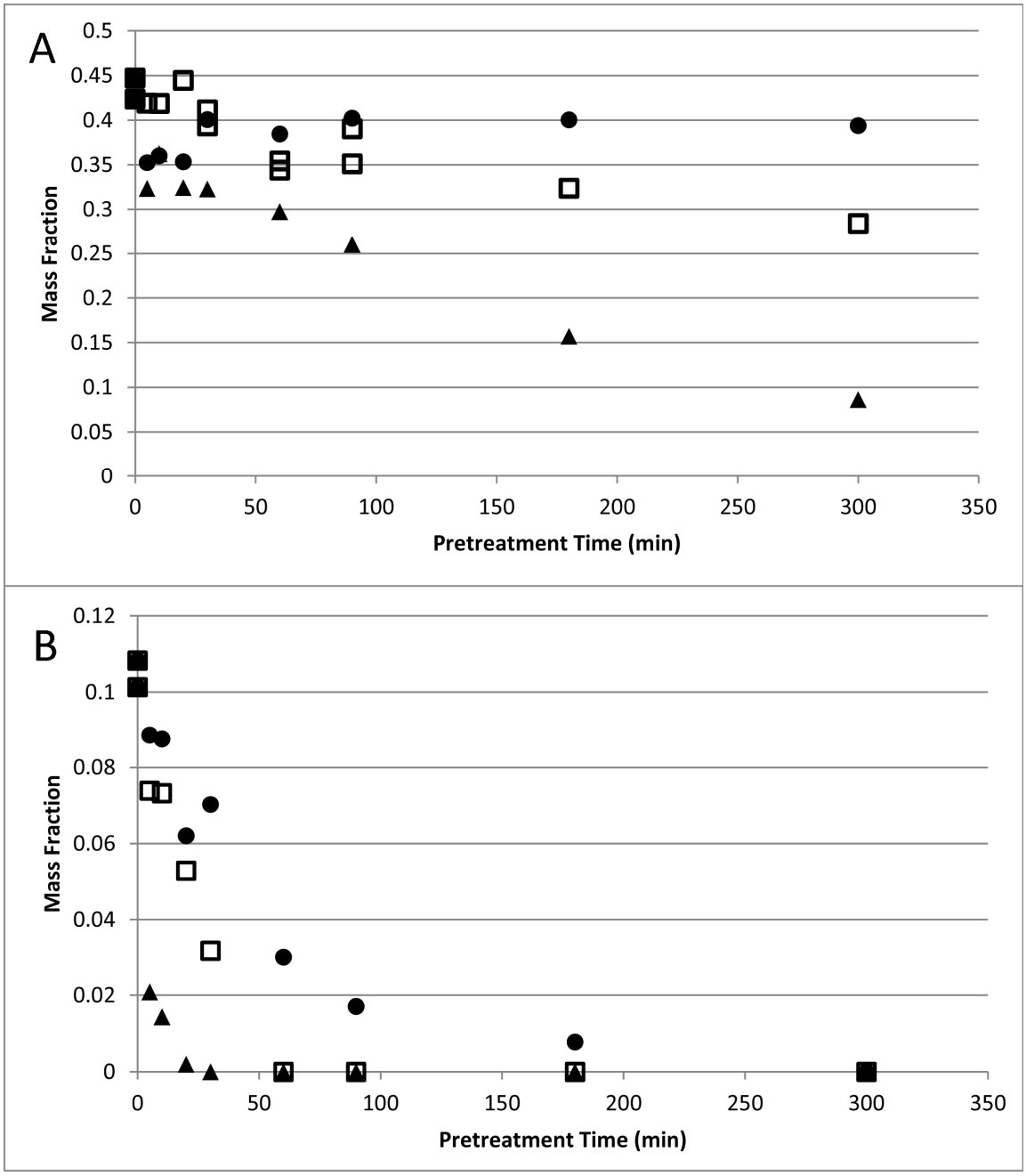

Figure 7.3: Mass fraction of A) glucose and B) mannose recovered from saccharification of Fraction 1 from pretreatments carried out at 110°C (●), 130°C (□), and 150°C (▲).

Previous research has demonstrated the ability of HMIMCl to catalytically depolymerize lignin model compounds and oak wood lignin under the same conditions used in this study [25], [27]. The relative size of lignin fragments recovered from the pretreatment of yellow pine wood was evaluated using gel permeation chromatography (GPC). Figure 7.4 shows the GPC data for the lignin recovered in Fraction 2 and of lignin recovered from yellow pine using EMIMAc at 110°C both before and after reaction at 130°C for 300 min. Even for short treatment times, the recovered lignin appears to have reached its minimum size, as the elution time of the peaks does not change significantly. The lack of larger lignin fragments in Fraction 2 indicates that the process of lignin extraction from wood in HMIMCl proceeds through a depolymerization reaction before being solubilized by the ionic liquid. At 110°C, the recovered lignin fragments are larger than lignin fragments recovered at 130 or 150°C, indicating that the depolymerization of the lignin is not as complete at the lower temperature. Interestingly, the final size of the lignin fragments after depolymerization of EMIMAc-extracted lignin is smaller than that of lignin from Fraction 2. It is possible that the lignin extracted using EMIMAc is not completely representative of the lignin in the wood and more susceptible to depolymerization than the bulk wood lignin. In the 110°C treatment, very little lignin was extracted, most likely due to slow reaction rates in depolymerizing the lignin. The lignin recovered from longer pretreatments at 110°C was also larger than lignin obtained from 130 or 150°C pretreatments. The most likely explanation for this is that the lignin does not depolymerize quickly at this temperature When the wood was treated at 150°C, the lignin extraction occurred more quickly. Interestingly, the size of the lignin

fragments became larger between the 180 and the 300 min treatment at 150°C (Figure 7.4D). This is most likely due to repolymerization between lignin fragments. The effect could have been exacerbated by the inclusion of polysaccharide degradation products that may be present in the Fraction 2 sample or coupled with the lignin. The difference in depolymerization rate and repolymerization of lignin fragments has been observed in previous work [25], [27].

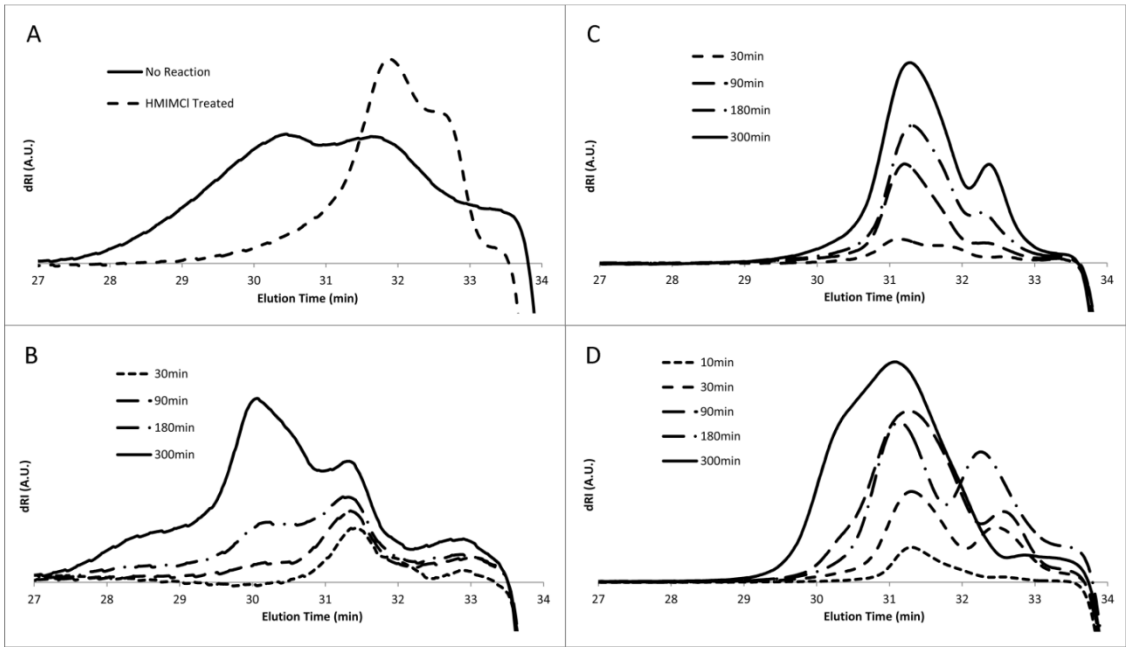

Figure 7.4: GPC results for the lignin recovered from A) EMIMAc-extracted lignin before and after treatment in HMIMCl at 130°C for 300min, B) Fraction 2 from pretreatments carried out at 110°C, C) Fraction 2 from pretreatments carried out at 130°C, and D) Fraction 2 from pretreatments carried out at 150°C.

To demonstrate that the HMIMCl treatment was effective as a pretreatment strategy for further processing, pretreated samples (10 mg) were reacted with cellulase from Trichoderma viride (3 ml of 34 unit ml-1 solution) for between 0 and 96 hr.

Samples from the 130°C treatment were chosen for cellulase digestion because treatment at this temperature removed significant amounts of lignin and hemicellulose over a relatively short period of time whereas treatment at 110°C did not remove much lignin and worked over too long as time span and 150°C treatments caused too much degradation of the cellulose. Figure 7.5 shows the mass of glucose recovered from wood treated with HMIMCl along with wood treated with EMIMAc as a comparison with a fitted exponential curve to guide the eye. The data from Figure 7.5, when compared with the data in Figure 7.2 and Figure 7.3, show that while digestion of hemicellulose may be important in this pretreatment strategy, the depolymerization and extraction of lignin is a more important driver of pretreatment efficacy. The ability of cellulase enzymes to hydrolyze the cellulose into glucose increases well past when no more mannose can be detected in treated wood samples. The glucose yield continues to increase even after the Fraction 2 mass recovery levels out. This indicates that the HMIMCl pretreatment has more effect on the wood than just the removal of hemicellulose and lignin. Previous reports have shown that ionic liquids can disrupt the structure of cellulose [31], [32], an effect that would explain this continued increase in glucose recovery. This is most likely the reason for the faster rate of saccharification in the EMIMAc treated samples. While the HMIMCl treated sample could yield higher glucose recovery, the EMIMAc treated samples were able to produce a lower yield faster. Mass transfer limitations resulting in incomplete dissolution of the wood in EMIMAc could be the cause for the lower glucose yield from the EMIMAc treated samples. As the glucose yield was still increasing with time after 96 hr, the total glucose yield for the HMIMCl pretreated samples would

continue to increase with longer digestion times. Longer digestions were not conducted due to the increased risk of microbial contamination and because the purpose of the digestions was to demonstrate the efficacy of the pretreatment and not to design an optimized glucose production method. This process was not optimized for either IL, so comparison of the HMIMCl and EMIMAc treatments may be misleading as a comparison of process viability. By milling the HMIMCl pretreated wood to increase surface area or additional treatment steps to further reduce cellulose crystallinity, the speed of saccharification could be enhanced.

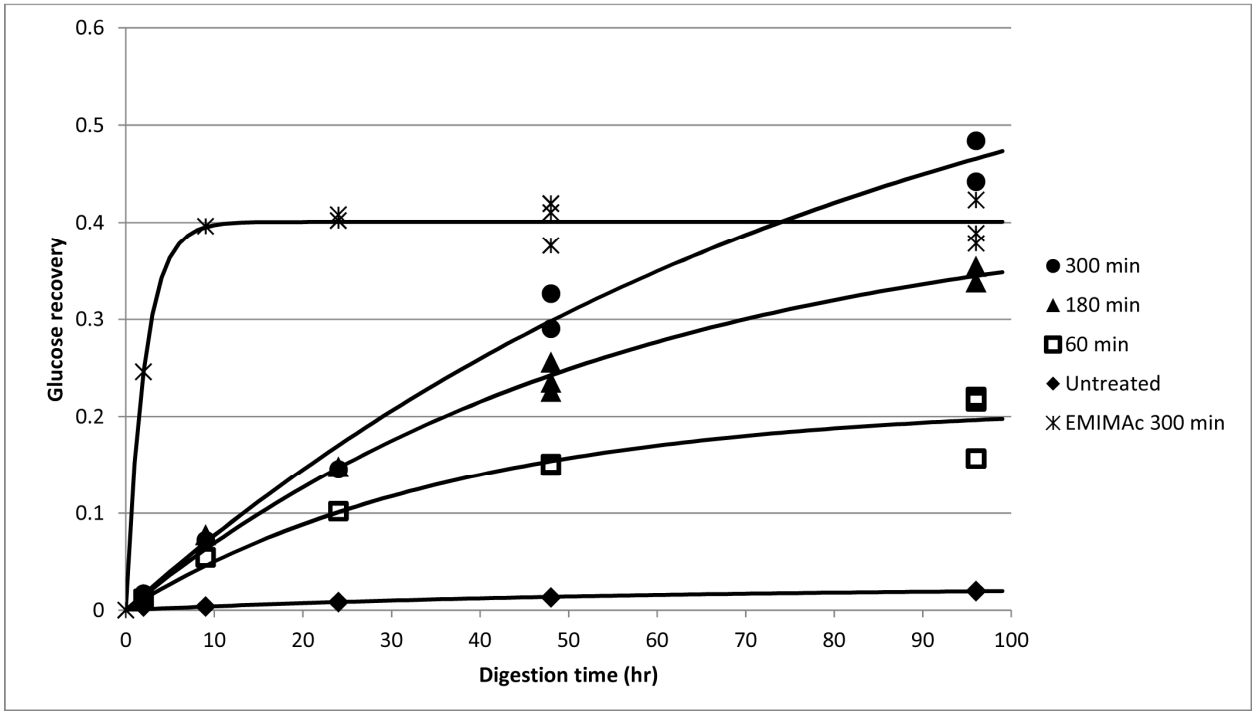

Figure 7.5: Glucose recovery from enzymatic digestion of untreated yellow pine (◆) and samples pretreated at 130°C for 60 (□), 180 (▲), 300 min (●), and 300 min in EMIMAc (✳). Glucose recovery is given as a mass fraction of the digested wood sample. The fitted curves are provided to guide the eye.

The products of hemicellulose degradation are not known. No clear identifications could be made of products in Fraction 3. Some of the products in this fraction are volatile and were collected *in vacuo* using a liquid nitrogen cold trap. Mass spectrometry analysis indicated that two masses present are 72 and 76 amu with secondary peaks that suggest the presence of an alcohol. Dehydration of six carbon sugars often results in the production of 5-(hydroxymethyl)furfural (HMF) [20], [33], although this product was not detected in significant amounts in samples tested using high pressure liquid chromatography (HPLC). Seivers et al. tested glucose and mannose for the production of HMF in an ionic liquid with added acid catalyst, but only achieved 12% yield with glucose and only "very small amounts" of HMF from mannose [34]. The reaction pathway for conversion of glucose and mannose into HMF requires isomerization to fructose, which does not occur at high yields without the addition of a catalyst [33]. Because the polysaccharides in hemicellulose are easily hydrolyzed under acidic conditions [9] and monosaccharides begin caramelizing at high temperatures, high ionic strength, and low pH, it is possible that the hemicellulose is being hydrolyzed into mono- and oligosaccharides and subsequently undergoing caramelization [35]. More research is needed to determine the reactions occurring in the hemicellulose and the products.

7.3 EXPERIMENTAL

7.3.1 Materials

1-H-3-methylimidazolium chloride (HMIMCl, ≥95%), 1-ethyl-3-methylimidazolium acetate (EMIMAc, ≥90%), cellulase (≥5 kU g-1), D(+)-mannose

(≥99%), 5-(hydroxymethyl)furfural (HMF, ≥99%) , D-manitol (≥98%), calcium carbonate (≥99%), and citric acid monohydrate (≥99.5%) were purchased from Sigma Aldrich. Acetone (99.7%), sulfuric acid (96.6%), dimethylsulfoxide (99.9%), dimethylsulfoxide-d6 (≥99.9%), and D-glucose (≥99%) were purchased from Fisher Scientific. Yellow pine wood chips were generously donated by KIOR, Inc. and kept in a vacuum oven at 60°C while not in use to maintain a consistent moisture level. Ionic liquids were dried at 100°C on a Schlenk line to a pressure of 100 mTorr. All other chemicals were used without further purification.

7.3.2 Pretreatment

In a typical pretreatment experiment, yellow pine wood chips (30 mg) were added to a glass reaction vial along with of deionized water (2.5 μl) and a stir bar. IL (1.0 ml), which was melted in a boiling water bath in the case of HMIMCl, was added to the reaction vial via pipette. The vial was sealed and inserted into a Thermo Scientific Reacti-Therm heated stirred reactor set to 110, 130, or 150°C. The samples were stirred for the prescribed time and then moved to a room temperature water bath to cool down for roughly 30 s. The sample was then mixed with a 1:1 solution of acetone and water (5 ml). The remaining solids were filtered using a 25 mm diameter glass fiber filter disk and washed twice with 1:1 acetone/water (2x 5 ml). The washed solids were then dried overnight (at least 8 hr) in a vacuum oven at 60°C to produce Fraction 1. The acetone in the remaining liquid was then evaporated at 40°C and using an aspirator to provide vacuum. Precipitated lignin was then filtered with a glass filter disk and washed twice

with deionized water (2x 5 ml). This solid was dried in a vacuum oven over night to yield Fraction 2. The remaining aqueous sample was Fraction 3.

In order to collect the volatile products from the treatment, the cooled sample was quenched with water instead of the 1:1 acetone/water. This quenched sample was then connected to a Schlenk line so all volatiles could be collected in a liquid nitrogen cold trap *in vacuo*. The collected liquid from the cold trap was diluted to 15 ml with deionized water and analyzed using HPLC or mass spectrometry.

7.3.3 Acid digestion

Fraction 1 samples were saccharified using the modified procedure published by the National Renewable Energy Lab [28]. The solids of Fraction 1, along with the glass fiber filter disk, were loaded in a 14 ml glass pressure tube. Sulfuric acid (72 wt%, 300 µl) was added to the pressure tube and the sample was stirred every 5 to 10 min at 30°C for 60 min. After the 60 min had elapsed, deionized water (8.4 ml) was added. The tube was sealed and allowed to react in an oven set at 121°C for 2 hr, then cooled to room temperature first in air and then with room temperature water. To each tube, calcium carbonate (700 mg) was added slowly to neutralize the sulfuric acid and precipitate calcium sulfate. The residual solids (calcium sulfate, lignin, and filter disk) were filtered and the liquid was analyzed using HPLC.

7.3.4 HPLC/GPC analysis

HPLC analysis was carried out using a Phenomenex Rezex RPM Monosaccharide Pb2+ 300 x 7.8 mm column held at 80°C with degassed, deionized water as an eluent and a

Wyatt Optilab T-Rex differential refractive index detector. Samples were prepared by mixing liquid from the sulfuric acid saccharification (200 μl), manitol solution (6.0 mg ml-1, 100 μl) as an internal standard, and deionized water (1700 μl). HPLC standards were produced by adding known amounts of glucose and mannose to pressure tubes and following the sulfuric acid saccharification procedure. The samples produced through this procedure allowed for quantification of recovered glucose and mannose and accounted for degradation of monosaccharides in the saccharification process.

GPC analysis was carried out on the same equipment as used for the HPLC using two Phenomenex Phenogel 5 μm linear/mixed 300 x 7.8 mm columns with DMSO as the eluent. Samples were prepared by adding DMSO (1.0 ml) to the filter disk with Fraction 2. This mixture was stirred until the solids from Fraction 2 had dissolved in the DMSO. The sample was then filtered and injected into the GPC without further dilution. The unreacted yellow pine lignin (5.2 mg) was dissolved in DMSO (1.0 ml) and filtered as a standard. The depolymerized lignin standard was created by subjecting EMIMAc-extracted lignin (11.9 mg) to a standard pretreatment in HMIMCl at 130°C for 300 min.

7.3.5 Lignin standard and NMR analysis

Unreacted lignin was extracted from yellow pine through a modified process developed by Sun et al. [29]. Dry yellow pine wood (2 g) was added to EMIMAc (28 g) and stirred at 110°C for 48 hr. The mixture was then quenched with 1:1 acetone/water (300 ml) and stirred for 3 hr. The mixture was filtered and the acetone evaporated. The

precipitated lignin was filtered, washed twice with 5 ml of deionized water, and dried *in vacuo* at room temperature.

The lignin standard was used for comparison in the GPC analysis and for NMR analysis. The NMR sample of unreacted lignin was made by dissolving EMIMAc-extracted lignin (19.3 mg) in DMSO-d6 (1.2 ml). An NMR sample for Fraction 2 was created by first running three standard pretreatment experiments at 130°C for 300 min, each with double the IL, wood, and water. The filter disks with Fraction 2 were stirred with DMSO-d6 (1.2 ml), and filtered to make the NMR sample.

7.3.6 Cellulase digestion

To test the efficacy of the pretreatment, Fraction 1 samples were digested with cellulase from Trichoderma viride using a method derived from that of Lee et al. [24]. A stock buffer solution was made by adjustiong the pH of a 50 mM citric acid solution to pH 4.7 using a concentrated sodium hydroxide solution. The buffer solution was boiled for 2 min and cooled to room temperature immediately prior to use. Then cellulase (5 unit mg-1) was dissolved in the citrate buffer to make a working solution (51 unit ml-1). The caps of the reaction vials were sterilized using ethanol and dried with flowing argon. In a typical digestion, treated wood (10 mg) and citrate buffer (1.0 ml) were added to a vial with a stir bar and placed in a boiling water bath for 3 min to sterilize the solution. Then the vials were cooled to room temperature and of the cellulase solution (2 ml) was added to each vial with a sterilized pipette tip to achieve 3 ml of 34 unit ml-1 solution. The mixture was then stirred at 37°C and allowed to react for 2, 9, 24, 48, or 96 hr. The

samples were then held in a boiling water bath for 3 min to quench the reaction by denaturing the enzymes. After filtering, the samples are analyzed with a YSI 7100 multiparameter bioanalytical system with a glucose sensor. Digestions of 48 hr and 96 hr were repeated three times. Samples with obviously low glucose yields were assumed to have been unintentionally inoculated with microorganisms and discarded.

7.4 CONCLUSION

The acidic ionic liquid 1-H-3-methylimidazolium chloride has been shown to be effective at pretreating yellow pine wood chips under mild conditions. When yellow pine is treated with HMIMCl, both the hemicellulose and the lignin are extracted. Both of these processes are reactive, given that the extracted lignin recovered from the treatment has already been depolymerized even at shorter reaction times. The hemicellulose is degraded into a number of unknown products, most likely through caramelization reactions. This pretreatment causes the yellow pine to be more prone to enzymatic attack, as demonstrated by cellulase digestion. While the removal of hemicellulose may be beneficial to the enzymatic digestion, the lignin extraction is the main driver of the efficacy of this pretreatment. Longer pretreatment times correlated to more complete and faster release of glucose from the cellulose digested with cellulase enzymes. Further research would be needed to optimize the process and determine the reactions occurring with the hemicellulose extraction.

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Chapter 8: Conclusions

8.1 Conclusions

The future of energy production will certainly include biomass as a renewable resource. Biomass derived products will also be important in the production of many other chemical commodities. Ionic liquids may become an important part of the technologies implemented to utilize these renewable resources. As both solvents and catalysts, ionic liquids have a unique set of properties that have distinct advantages over more traditional methods of biomass processing. The ability to solubilize lignocellulose opens up a wide range of chemical processes that are otherwise difficult or impossible to achieve with biomass using conventional methods. Additionally, catalysis and post reaction separations can often be enhanced through the use of ionic liquids. While there are many benefits to using ionic liquids, there are also a number of challenges that need to be overcome if ionic liquids are to be used in the next generation of biomass processing technologies. Recycling of ionic liquids is of paramount importance because ionic liquids are significantly more expensive than conventional solvents. This requires effective separations of biomass products from the ionic liquids and ionic liquids from any other co-solvents used in the process. Overall, the advantages that can be realized through the use of ionic liquids continue to drive research in overcoming the challenges and developing new ways to take advantage of the benefits.

Even though base catalyzed depolymerization of lignin is one of the most widely used technologies in the pulp and paper industry [1], base promoted delignification in ionic liquids does not show much promise. The trialkylimidazolium chloride, 1-butyl-2,3-dimethylimidazolium chloride (BDMIMCl), was required to accommodate the highly basic conditions. Unfortunately, use of this ionic liquid reduces the solubility of biomass in the ionic liquid. Additionally, the base promoted depolymerization of lignin in ionic liquids could not be made catalytic under the conditions that were tested. Only one of the tested bases, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), was effective at cleaving the ether linkage in the lignin model compounds. This polycyclic nitrogen compound is a super base, meaning it is more strongly basic than the hydroxide anion. While there may be some interesting chemistries that could be conducted through base catalyzed methods in ionic liquids, it is unlikely that base promoted cleavage of ether linkages in lignin in ionic liquids would be effective on an industrial scale.

As a workable method for lignin depolymerization, treatment with acidic ionic liquids as both catalyst and solvent has significantly more promise than base promoted depolymerization. Lignin is hydrolyzed easily under mild conditions in a simple system consisting of HMIMCl, a small amount of water, and lignin. This process could be used as a method for recovering lignin from biomass feedstock through reactive lignin extraction. Compared to methods given in the literature, the extraction of lignin from wood is significantly faster using HMIMCl than when using a neutral IL such as 1-ethyl-3-methylimidazolium acetate. The ionic liquid is reusable and, although not inexpensive, less costly than many other ionic liquids that have been tested in the treatment of

biomass. There are a few shortcomings to this method for depolymerization. The lignin fragments produced are not monomeric, as the acid catalyzed hydrolysis does not break the C-C linkages in the lignin macromolecule. Consequently, if the lignin extracted from biomass with HMIMCl was to be used for aromatic feed stocks, further processing would be needed to make small, deoxygenated molecules.

The pretreatment of biomass using HMIMCl is an effective use of this technique. The ionic liquid quickly removes the lignin and hemicellulose from pine wood, opening the cellulose structure for saccharification by cellulase enzymes. Interestingly, HMIMCl does not dissolve cellulose, most likely due to the strong hydrogen bonding ability of the cation. This puts HMIMCl at a disadvantage to other ionic liquids such as EMIMAc and 1-butyl-3-methylimidazolium chloride (BMIMCl) that solubilize the entirety of the biomass, disrupting the crystallinity of the cellulose in the process. The HMIMCl, however, is more effective at removing the lignin and hemicellulose from the sample, creating a more cellulose rich substrate for saccharification. Further research is needed to fully understand the positive and negative aspects associated with various ionic liquids as a means to pretreat biomass for saccharification.

There is potential for this technology to provide substantial benefits for the processing of biomass, although more work can be done to find the best ionic liquids, processes and conditions to use. Pretreatment is one of the most promising of these avenues. More research could be done into the right kinds or even combinations of ionic liquids. Once the most advantageous system for pretreatment has been found, there is much work that must be done in scale up. Very few processes with ionic liquids have

been expanded from bench top scale into pilot or industrial scale processes, none of which involve biomass processing. Difficulties in separations, efficient recycle, and equipment design will need to be addressed. Especially if soluble saccharides are produced, recovery of all the processed biomass is an area that requires attention. Efficient ionic liquid recovery is also a topic that requires further research, as the most general method seen in the literature involves the use of antisolvents that must be distilled from the ionic liquid later in the process. This method is ultimately energy intensive and requires the use of volatile solvents, so alternative methods for separations and ionic liquids recovery are an important area of research.

Expanding on the idea of pretreatment for saccharification, it may be possible to combine the pretreatment and saccharification steps. Some ionic liquids have been designed that do not denature lipase enzymes in solution while still dissolving lignocellulose, allowing for homogenous enzymatic modification of cellulose [2]. If cellulase enzymes could maintain activity when added to an ionic liquid, saccharification of the carbohydrates in biomass could happen in one step instead of two. The separations of the monosaccharides from the ionic liquid phase would still be an issue, unless the next stage in processing could be done in the ionic liquid phase as well.

Other work also needs to be done in utilization of recovered lignin fragments from biomass treatment. Ionic liquids hold promise for this line of research, because lignin is soluble in a wide range of ionic liquids [3]. Hydrodeoxygenation is difficult in ionic liquids due to the thermal limitations of the required catalysts and the ionic liquids. More novel ionic liquids, such as the dicationic imidazolium chlorides that have been

shown to work as a medium for cellulose pyrolysis, could be a solution for this problem, as they have a higher thermal stability that conventional imidazolium based ionic liquids [4]. Other possibilities, such as chemical modification of lignin fragments in ionic liquids could be explored. There has been significant research into modification of cellulose and monosaccharides in ionic liquids [5], but very little, if any, into modification of lignin under the same conditions. The lignin fragments recovered from pretreatment could also be fed into more conventional processing techniques, such as gasification or pyrolysis processes.

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Vita

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He then started his graduate work at the University of Texas at Austin. Under the direction of Dr. John Ekerdt, Blair and a visiting researcher from China, Songyan Jia, started a biomass catalysis project that relied on the unique properties of ionic liquids. Over this time, Blair published two first author publications and was second author on three others. At the time of the writing of this dissertation, he had one more journal article and a book chapter on biomass catalysis in ionic liquids that had not yet been published.

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